J. Phys. Chem. B **2004,** *108,* 17261−17268

Stable Charge-Transfer Complexes versus Contact Complexes. Application to the Interaction of Fullerenes with Aromatic Hydrocarbons

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Received: July 6, 2004; In Final Form: August 21, 2004

The methods of calculation of the equilibrium constants and electronic absorption spectra of charge-transfer complexes are discussed with special emphasis on the treatment of the contact interaction. In particular, a model for the pseudo-equilibrium of contact complexes is developed. It is shown that a small but nonzero effective equilibrium constant can be defined for contact pairs and all higher order contact complexes. The results are applied to the study of the interaction of C_{60} and C_{70} with naphthalene and 1-methylnaphthalene, with the main goal being to establish the nature of the interaction of the fullerenes with these aromatic hydrocarbons. It is concluded that only simple contact complexes are formed, for which several spectroscopic parameters are obtained.

1. Introduction

Charge-transfer (CT) bands in electronic absorption spectra are often observed in solutions where the solvent−solute interaction is of the donor−acceptor type. They are also observed when a suitable donor−acceptor pair is dissolved in an inert solvent. However, the existence of a CT band does not imply the existence of a stable charge-transfer complex. Essentially unbound molecular pairs, the so-called contact pairs (which could also be called physical complexes), may also display a modified absorption spectrum, including the appearance of one or more broad, structureless CT bands.[1−3] The binding energy of contact pairs is negligible, that is, smaller than the thermal agitation energy ($RT \cong 3$ kJ mol^{-1} at 300 K), and the apparent formation equilibrium constant K is very small (typically between 0.1 and 1 M^{-1}, see Section 3) and temperature independent. However, for stable ground-state CT molecular complexes, the binding energy is significant and the formation equilibrium constant is much larger than the statistical pair value, decreasing with a temperature increase according to the van't Hoff equation.

The existence of CT bands in the absorption spectrum of the contact pair implies that, unlike the ground state, some of its excited states have a significant binding energy. When the lowest excited state is bound, one can speak of an exciplex. However, it may also happen that the lowest excited state of the contact pair is of the locally excited (LE) type, the excitation being mainly localized in the donor or in the acceptor. In such a case, all CT bands correspond to transitions to higher excited states.

There are, therefore, two types of contact pairs: (i) Those that form exciplexes (exciplex forming contact pairs), whose lowest CT band corresponds to a transition to the first excited state; and (ii) Those that do not form exciplexes, whose CT bands correspond to transitions to higher excited states (simple contact pairs). We note that the energy of (emissive) exciplexes is defined by the relevant band in the observed fluorescence spectrum whose frequency corresponds to the relaxed geometry of the excited complex and not to that of the Franck−Condon state relevant for absorption.

Despite extensive π-electron delocalization, fullerenes are electron-deficient species,[4] acting as electron acceptors (A) and giving rise to charge-transfer bands when interacting with a variety of electron donors (D), including amines[5−19] and aromatic hydrocarbons.[20−25] A striking manifestation of the different behavior displayed by fullerenes and by aromatic hydrocarbons toward electron acceptors is the lack of fluorescence quenching of a C_{60} dendrimer by Cs^+,[26] whereas this same cation efficiently quenches a number of aromatic hydrocarbons by the external heavy-atom effect. In the case of excited-state fullerenes, mixing of the wave functions by charge-transfer to Cs^+ is not effective.

The first studies of ground-state CT interactions of fullerenes with amines (*N*,*N*-dimethylaniline, DMA, and *N*,*N*-diethylaniline, DEA) were reported by Hochstrasser and co-workers[5] and by Wang.[6] More recently, additional studies with aromatic and aliphatic amines were published.[7−19] In all cases, owing to the formation of CT complexes, a progressive increase in the intensity of the lowest energy absorption band with increasing amine concentration was reported. The changes in the electronic absorption spectrum of the mixture are much greater for C_{60} than for C_{70}.[17] The C_{60}−DEA CT band has a maximum located at 564 nm, with a molar absorption coefficient of 20 000 M^{-1} cm^{-1}.[15] Measured equilibrium constants are small and relatively similar, falling between 0.04 and 0.4 M^{-1} for C_{60}. For the C_{70}−DEA complex in methylcyclohexane (MCH), Wang[5] reported an equilibrium constant of 0.4 M^{-1}, whereas Bhattacharya et al.[19] recently obtained 1.2 M^{-1} for the same pair in CCl_4, and values between 2.3 and 2.6 M^{-1} for substituted anilines in the same solvent.

Various aspects of fullerene donor−acceptor interaction with aromatic hydrocarbons have also been studied.[8,20−25,27] Rao et al.[8] first postulated a very weak ground-state interaction of C_{60} and C_{70} with benzene and estimated an equilibrium constant of 0.2 M^{-1} in MCH. However, no CT band was identified. The CT interaction of C_{60} with substituted naphthalenes was studied by Ogilby et al.,[20] who reported a very weakly bound or essentially unbound ground-state CT complex with a small equilibrium constant of 0.08 ± 0.02 M^{-1} for the C_{60}−1-methylnaphthalene (MN) complex in toluene. The C_{60}−MN

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10.1021/jp047019z CCC: $27.50

complex CT band has a maximum located at 425 nm, with a molar absorption coefficient of 11 000 M^{-1} cm^{-1}.[20] Later, Sibley et al.[21] studied the interaction of C_{60} with polycyclic aromatic hydrocarbons, reporting $K = 0.1$ M^{-1} for the C_{60}−naphthalene complex and increasing values by an order of magnitude as the number of aromatic rings of the donor is increased. The measured enthalpies of complex formation[21] that were obtained from van't Hoff plots are nevertheless dubious because they are always smaller than RT. All of these results point to CT associations essentially of the contact type, although this has not been explicitly recognized by a majority of the authors. In contradiction with these results, substantially larger equilibrium constants were recently reported for the same C_{60} systems with values ranging from 0.7 to 66 M^{-1}, depending on the number of aromatic rings of the donor.[22] In another study,[27] the same authors claim to have identified CT bands in the spectrum of C_{60} dissolved in a number of benzene liquid derivatives and report very small equilibrium constants (0.1 to 1.2 M^{-1}) but, surprisingly, very significant enthalpies of complex formation (−29 to −98 kJ mol^{-1}). Again, in a study of the charge-transfer interaction of C_{70} with aromatic hydrocarbons, Bhattacharya et al.[25] report high equilibrium constants with values ranging from 11 to 490 M^{-1}, and significant formation enthalpies with values ranging from −21 to −66 kJ mol^{-1}.

The purpose of this work is two fold: First, the methods of calculation of equilibrium constants and electronic absorption spectra of charge-transfer pairs are discussed, with special emphasis on the treatment of contact pairs; in particular, a new model for the pseudo-equilibrium of contact pairs and higher complexes is developed. It is shown that a small but nonzero effective equilibrium constant characterizes contact complexes; Second, the derived results are applied to the study of the interaction of C_{60} and C_{70} with aromatic hydrocarbons, namely, naphthalene, 1-methylnaphthalene (MN), and anthracene, for which there are conflicting results in the literature.

2. Experimental Section

C_{60} (>99.9%) and C_{70} (>99.9%) were purchased from Aldrich and used as received. Naphthalene (Fluka) and anthracene (Aldrich) were also used as received. 1-methylnaphthalene (Fluka) was purified by passing through a silica gel column prior to use. Toluene (Merck), MCH (Aldrich), and CCl_4 (Fluka) were of spectroscopic grade. Absorption spectra were recorded on a Shimadzu UV-3101PC UV−vis−NIR spectrophotometer with variable temperature cell holders using 1.0-cm path length cells. The temperature was controlled with a circulating bath and measured inside the cells with a thermocouple. All spectra were run against blank solutions with matching donor concentrations, thus accounting for the possibility of residual donor absorption. The concentration dependence of the absorption spectra of the mixtures was used to quantify the interaction of C_{60} and C_{70} with naphthalene and 1-methylnaphthalene in two different solvents, toluene and CCl_4. The donor concentration was varied between 0.8 and 1.8 M for naphthalene and between 0.1 and 3.6 M for MN. The C_{60} and C_{70} concentrations were kept fixed at 2×10^{-4} and 2×10^{-5} M, respectively.

3. Results and Discussion

3.1. Formalism and Methods of Data Analysis. The formation of 1:1 donor−acceptor CT complexes DA

$$\mathrm{D} + \mathrm{A} \rightleftarrows \mathrm{DA} \tag{1}$$

has an associated concentration equilibrium constant

$$K = \frac{[\mathrm{DA}]}{[\mathrm{D}][\mathrm{A}]} \tag{2}$$

We will always assume, as is usually done in the treatment of CT complexes, that K is only a function of temperature, that is, it is proportional to the true (thermodynamic) equilibrium constant written in terms of activities.

Spectrophotometric studies for the evaluation of K are usually carried out with a small and fixed concentration of D or A and varying the concentration of the other partner in the complex, usually in large excess. In the following, it is always assumed that A (fullerene) is fixed and at low concentration and that D (aromatic hydrocarbon) is in large excess.

Considering first a wavelength where only the complex DA absorbs, the absorbance is

$$\mathrm{A} = \epsilon_{\mathrm{CT}}[\mathrm{DA}]l = \epsilon_{\mathrm{CT}}\, l\, \frac{K[\mathrm{A}]_0[\mathrm{D}]_0}{1 + K[\mathrm{D}]_0} \tag{3}$$

where ϵ_{CT} is the molar absorption coefficient of the complex, l is the optical path length, $[\mathrm{A}]_0$ is the analytical (total) concentration of acceptor, and $[\mathrm{D}]_0$ is the total concentration of donor. The unknowns are ϵ_{CT} and K.

Equation 3 can be rewritten as

$$\mathrm{A} = \frac{A_\infty[D]_0}{\dfrac{1}{K} + [\mathrm{D}]_0} \tag{4}$$

where A_∞ is the absorbance when $[\mathrm{D}]_0 \rightarrow \infty$

$$A_\infty = \epsilon_{\mathrm{CT}}[\mathrm{A}]_0 l \tag{5}$$

From eq 4, it is clear that to obtain K with reasonable accuracy the denominator can be neither very close to $^1/_K$ nor very close to $[\mathrm{D}]_0$. This forms the basis of a well-known criterion, due to Person,[28] according to which the range of useful donor concentrations is $^{0.1}/_K < [\mathrm{D}]_0 < {}^9/_K$.

Equation 3 is traditionally used in one of the following linearized forms

$$\frac{[\mathrm{A}]_0 l}{\mathrm{A}} = \frac{1}{\epsilon_{\mathrm{CT}}} + \frac{1}{\epsilon_{\mathrm{CT}} K[\mathrm{D}]_0} \tag{6}$$

$$\frac{[\mathrm{A}]_0[\mathrm{D}]_0 l}{\mathrm{A}} = \frac{1}{\epsilon_{\mathrm{CT}} K} + \frac{[\mathrm{D}]_0}{\epsilon_{\mathrm{CT}}} \tag{7}$$

$$\frac{\mathrm{A}}{[\mathrm{D}]_0 l} = \epsilon_{\mathrm{CT}} K[\mathrm{A}]_0 - K\mathrm{A} \tag{8}$$

that are known as the Benesi−Hildebrand (BH), Scott, and Foster−Hammick−Wardley (FHW) equations, respectively.[29] Although still widely found in the current literature, there seems to be little justification for the present use of these methods, given that software for nonlinear least squares is readily available. Nonlinear analysis avoids the introduction of point-dependent statistical weights, mandatory in a proper, but seldom done, least-squares treatment of linearized data. Equations 6−8 should preferably be used only for obtaining initial estimates of ϵ_{CT} and K, necessary in the nonlinear fit according to eq 4, rewritten as

$$\mathrm{A} = \frac{a[\mathrm{D}]_0}{b + [\mathrm{D}]_0} \tag{9}$$

with a and b being the fitting parameters.

Consider now a wavelength where both A and the complex DA absorb. Instead of eq 3, one has

$$A = \epsilon_A[A]l + \epsilon_{CT}[DA]l = A_0 \frac{1 + K'[D]_0}{1 + K[D]_0} \qquad (10)$$

where

$$A_0 = \epsilon_A[A]_0 l \qquad (11)$$

is the absorbance in the absence of donor, and K' is

$$K' = \frac{\epsilon_{CT}}{\epsilon_A}K = \alpha K \qquad (12)$$

A plot of A/A_0 thus enables the determination of ϵ_{CT} and K as

$$\frac{A}{A_0} = \frac{\frac{1}{K} + \alpha[D]_0}{\frac{1}{K} + [D]_0} \qquad (13)$$

Person's restrictions on the concentration of the donor still apply here. Nevertheless, a supplementary condition exists, namely, that α cannot be close to 1. Assuming that $\alpha > 1$ and writing $\alpha = 1 + \beta$, eq 13 becomes

$$\frac{A}{A_0} = 1 + \frac{\beta[D]_0}{\frac{1}{K} + [D]_0} \qquad (14)$$

Person's criterion imposes ${}^{0.1}/_{K} < [D]_0 < {}^{9}/_{K}$. Additionally, the second term of the rhs of eq 14 cannot be much smaller than 1, say, it must be higher than 0.1. One thus obtains that $\beta > 1/([D]_0K)$ or that

$$[D]_0 > \frac{1}{(\alpha - 1)K} \qquad (15)$$

If $\alpha > 11$, then Person's range of concentrations remains valid. If, however, $1.1 < \alpha < 11$, then the permissible range of concentrations is reduced, as the lower limit for the concentration of the donor, given by eq 15, is higher than $0.1/K$. Finally, if $\alpha < 1.1$, then the spectral changes for the entire Person's concentration range are very small, and the method is not applicable.

Equation 10 can also be linearized, for instance, the equivalent of the BH equation, sometimes called Ketelaar equation,[29] is

$$\frac{[A]_0 l}{A - A_0} = \frac{1}{\epsilon_{CT} - \epsilon_A} + \frac{1}{(\epsilon_{CT} - \epsilon_A)K[D]_0} \qquad (16)$$

For the linearizations analogous to eqs 7 and 8, it suffices to substitute in these equations $\Delta A = A - A_0$ for A and $\Delta\epsilon = \epsilon_{CT} - \epsilon_A$ for ϵ_{CT}. Again, these linearized forms are best used only for obtaining initial estimates of ϵ_{CT} and K, to be employed in conjunction with eq 13, rewritten as

$$\frac{A}{A_0} = \frac{a + b[D]_0}{a + [D]_0} \qquad (17)$$

with a and b being the fitting parameters.

Once the equilibrium constant K has been determined, the absorption spectrum of the CT complex can be obtained from eq 13, rewritten as

$$\epsilon_{CT}(\lambda) = \frac{1}{[A]_0 l}\left\{\frac{1}{K[D]_0}[A(\lambda) - A_0(\lambda)] + A(\lambda)\right\} \qquad (18)$$

The spectrum of the CT complex is frequently discussed on the basis of the difference spectrum between the D + A solution, where the concentration of free A is [A], and the pure A solution (concentration $[A]_0$), that is $A(\lambda) - A_0(\lambda)$. Although this procedure certainly evidentiates the spectral changes accompanying complexation, it is incorrect because it implicitly assumes that in the D + A solution the concentration of A in the complexed form is negligible, which is not usually the case, cf. eq 18.

Note also that, because K is indirectly evaluated from measurements of the absorption spectrum, if there is a solvent effect on the CT absorption, then K may not be independent of [D] as assumed. It is therefore important to compute the spectrum of the complex for several concentrations of D, to confirm that it is essentially independent of [D].

3.2. Contact Charge-Transfer Pairs. *Isotropic Interaction.* As will be shown, contact pairs are characterized by an apparent equilibrium constant, although no true chemical equilibrium exists. This apparent constant can be estimated according to a simple model that is now presented.

Suppose that A and D are solutes, whose molecules are spheres of radii R_A and R_D, respectively, immersed in a solvent continuum. Suppose further that the concentration of D is much larger than that of A. If the DA complex is defined as the entity made up by the joined spheres, with a center-to-center distance of $R_c = R_A + R_D$ (collision diameter), and if the complex is formed only by chance (statistical pair), then the fraction of A molecules present as the contact pair is always negligible, except for very concentrated solutions of D, where most of the spheres are forced to be in permanent contact. This happens because for relatively dilute solutions, the probability of finding a D molecule in contact with an A molecule is essentially zero (it is the probability of a single value out of a continuous distribution).

If, however, the complex is defined as a somewhat more loose entity, for which the center-to-center distance is contained between R_c and $R_c+\Delta R$, then a finite fraction of pairs will exist in the form of contact pairs. This second definition of statistical pairs is more appropriate, given the range of distances that lead to the contact CT band(s). If ΔR is written as $\Delta R = \beta R_c$, then the volume of the spherical shell around A that can be occupied by the center of a D molecule is

$$v = \frac{4}{3}\pi\beta(3 + 3\beta + \beta^2)R_c^3 \qquad (19)$$

For β equal to $2^{1/3} - 1 = 0.26$, for instance, the volume becomes $v = (4/3)\pi R_c^3$. The probability of finding a A molecule with a nearby D molecule, with a center between R_c and $R_c + \Delta R$, will thus be $N_D v/V$, where N_D is the total number of D molecules, and V is the volume of the solution. This probability can be rewritten as $[D]N_A v$ or $[D]V_m$, where N_A is Avogadro's constant and V_m is a molar volume, $V_m = vN_A$. In this way, the number of A molecules present as complexes is $[D]V_mN_A$, and that present as free A molecules is $(1 - [D]V_m)N_A$. The corresponding molar concentrations are then $[D]V_m[A]$ and $(1 - [D]V_m)[A]$, respectively. If the possibility of complexes with two or more D molecules is to be discarded, then one must have $[D]V_m \ll 1$ and the concentrations of complexed and free A molecules become (approximately) equal to $[D]V_m[A]$ and [A]. The apparent equilibrium constant for the formation of the complex is therefore

$$K = \frac{V_m[D][A]}{[D][A]} = V_m \qquad (20)$$

The model allows for an estimate of the value of the equilibrium constant of a contact pair: For C_{60} and C_{70}, a van der Waals radius of 0.53 nm is appropriate. By taking a benzene molecule as the donor and assuming a ring−ring sandwich-type configuration for the contact pair, a van der Waals radius of 0.18 nm is used for benzene. Hence, $R_c = 0.71$ nm. In this way, eq 18 gives $V_m/M^{-1} = 0.90\beta(3 + 3\beta + \beta^2)$. Assuming that $\Delta R = 0.1$ nm, it follows that $\beta = 0.14$, and one obtains $K = V_m = 0.44$ M^{-1}. This simple model shows that equilibrium constants for contact pairs should fall roughly in the range 0.1 to 1 M^{-1}, in reasonable agreement with a previous estimate based on even cruder approximations.[30] For highly anisotropic interactions, one can nevertheless expect smaller K values because not all relative orientations will be adequate for the CT interaction.

The above results show that the long-standing and commonly held belief[1,2,29,31] that contact pairs have $K = 0$ is not correct. The contact pair is in fact characterized both by an effective, nonzero equilibrium constant and by a finite molar absorption coefficient ϵ_{CT}.

A full treatment of the contact interaction must take into account the possibility of formation of the complexes D_nA, with $n > 1$. Only when these are included does a coherent picture (effective multiple equilibrium) emerge. In fact, for sufficiently concentrated solutions, precisely those for which the contact CT pairs are observable, there is the possibility of contact associations of the type D_nA with $n > 1$ and up to a maximum coordination number N. In the case of fullerene−aromatic hydrocarbons systems, simple steric considerations lead to a maximum number of donors around the fullerene of 20 or more. Indeed, considering only the possibility of direct $\pi-\pi$ interaction between a benzene ring and a hexagon of the fullerene, there are 20 (C_{60}) or 25 (C_{70}) potential CT sites on each fullerene molecule.

Neglecting D−D interactions, the distribution of complexes, valid for the entire concentration range, follows the binomial law

$$P(n) = \frac{[D_nA]}{[A]_0} = \binom{N}{n}\left(\frac{\bar{n}}{N}\right)^n\left(1 - \frac{\bar{n}}{N}\right)^{N-n} \qquad (21)$$

where *P(n)* is the probability (fraction) of the acceptor A being in the form of a complex D_nA (including the free molecule, $n = 0$), $\bar{n} = V_m[D]_0 = K[D]_0$ is the average number of donors in contact with a generic A molecule, $N \approx K[D]_{max}$ is the maximum coordination number, and $[D]_{max}$ is the concentration of the donor in a pure donor medium (e.g., pure liquid). This distribution is plotted in Figure 1 for a hypothetical case where $K = 1$ M^{-1} and $[D]_{max} = 7$ M, implying that $N = 7$.

Every complex D_nA has an associated effective equilibrium constant, K_n, given by

$$K_n = \frac{[D_nA]}{[D]^n[A]} = \binom{N}{n}\left(\frac{V_m}{N}\right)^n \qquad (22)$$

These constants can be obtained from a multi-equilibrium mechanism whose elementary kinetic steps are

$$D_{n-1}A + D \underset{nk_{-d}}{\overset{\left[1-\frac{(n-1)}{N}\right]k_d}{\rightleftharpoons}} D_nA \qquad (n = 1, 2, ..., N) \qquad (23)$$

where the rate constants k_d and k_{-d} correspond to the pair diffusion-controlled association and dissociation, respectively. For the complex $D_{n-1}A$ the association rate constant is lower than k_d by a statistical factor $1 - (n - 1)/N$, given that $n - 1$ out of N potential sites are already filled with D molecules. For the complex D_nA, the dissociation rate constant is higher than k_{-d} by a statistical factor n, given that there are n molecules of D in the complex that can independently dissociate.

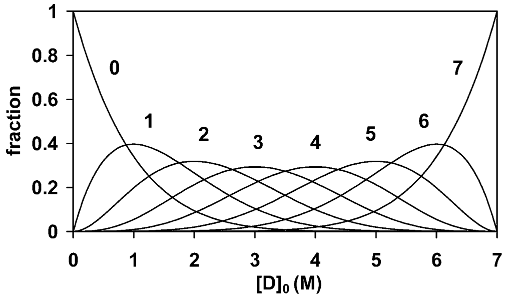

Figure 1. Fraction *P(n)* of the complexes D_nA ($n = 0, 1, ..., 7$) as a function of the donor concentration, for a hypothetical system with $K = 1$ M^{-1} and $[D]_{max} = 7$ M. The value of n is given next to each curve.

The above derivation shows that for contact complexes the apparent equilibrium constant is temperature independent. This is expected because the enthalpy of complexation is essentially zero.

Assuming that all contact complexes have a common molar absorption coefficient ϵ_{CT}, the absorbance at a wavelength where only the CT band is observed is given by

$$A = \epsilon_{CT}\sum_{n=1}^{N}[D_nA]l = \epsilon_{CT}\,l\,[1 - P(0)][A]_0 \qquad (24)$$

or

$$A = \epsilon_{CT}l\left[1 - \left(1 - \frac{\bar{n}}{N}\right)^N\right][A]_0 = \epsilon_{CT}l\left[1 - \left(1 - \frac{K[D]_0}{N}\right)^N\right][A]_0 \qquad (25)$$

For large N, and for $[D]_0 \ll [D]_{max}$, eq 25 reduces to

$$A = \epsilon_{CT}\,l\,[1 - \exp(-K[D]_0)][A]_0 \qquad (26)$$

which for relatively small $[D]_0$ yields

$$A = \epsilon_{CT}\,l\,K[A]_0[D]_0 \qquad (27)$$

This linear dependence of the absorbance with $[D]_0$ also follows from eq 3. For small K, it can be obeyed up to very high concentrations of D, but it does not imply that $K = 0$, as previously assumed by several authors.[1,2,29,31]

For a wavelength where A also absorbs, eqs 25 and 26 become

$$A = \epsilon_A l\left(1 - \frac{K[D]_0}{N}\right)^N[A]_0 + \epsilon_{CT}l\left[1 - \left(1 - \frac{K[D]_0}{N}\right)^N\right][A]_0 \qquad (28)$$

$$A = \epsilon_A\,l\,\exp(-K[D]_0)[A]_0 + \epsilon_{CT}\,l\,[1 - \exp(-K[D]_0)][A]_0 \qquad (29)$$

Equation 29 can be rewritten as

$$\frac{A}{A_0} = \exp(-K[D]_0) + \alpha[1 - \exp(-K[D]_0)] \qquad (30)$$

where α is defined by eq 12.

If it is now instead assumed that the molar absorption coefficient of the complex D_nA is given by n times ϵ_{CT}, then the absorbance at a wavelength where only the CT band is observed is given by (compare eq 27)

$$A = \epsilon_{CT}\sum_{n=1}^{N} n[D_nA]\,l = \epsilon_{CT}\,lK[A]_0[D]_0 \tag{31}$$

and a linear dependence of the absorbance with $[D]_0$ is obeyed for the entire donor concentration range. As before, this linear dependence does not imply that $K = 0$.

For a wavelength where the acceptor also absorbs, eq 31 becomes

$$A = \epsilon_A l\left(1 - \frac{K[D]_0}{N}\right)^N [A]_0 + \epsilon_{CT}\,lK[A]_0[D]_0 \tag{32}$$

an equation that is to be contrasted with eq 28.

3.3. Contact Charge-Transfer Pairs. *Anisotropic Interaction.* A more realistic model should include the possibility of anisotropic interactions. These can be approximately included in the previous model by considering that only a fraction p of all DA pairs has a favorable orientation and can give rise to a CT band. For D_nA complexes, the fraction with at least one DA pair favorably oriented is given by $1 - (1 - p)^n$. Assuming that all contact complexes with at least one DA pair favorably oriented have a common molar absorption coefficient ϵ_{CT}, the absorbance at a wavelength where only the CT band is observed is given by

$$A = \epsilon_{CT}\,l\left[1 - \left(1 - p\frac{\bar{n}}{N}\right)^N\right][A]_0 = \epsilon_{CT}\,l\left[1 - \left(1 - \frac{pV_m[D]_0}{N}\right)^N\right][A]_0 \tag{33}$$

Therefore, a spectrophotometric study will give an effective equilibrium constant of $K = pV_m$ for the DA pairs.

For a wavelength where the acceptor also absorbs, eq 33 becomes

$$A = \epsilon_A l\left(1 - \frac{V_m[D]_0}{N}\right)^N [A]_0 + \epsilon_A l\sum_{n=1}^{N}(1-p)^n\binom{N}{n}\left(\frac{V_m[D]_0}{N}\right)^n \left(1 - \frac{V_m[D]_0}{N}\right)^{N-n}[A]_0 + \epsilon_{CT}\,l\left[1 - \left(1 - \frac{pV_m[D]_0}{N}\right)^N\right][A]_0 \tag{34}$$

or

$$A = \epsilon_A l\left(1 - \frac{pV_m[D]_0}{N}\right)^N [A]_0 + \epsilon_{CT}\,l\left[1 - \left(1 - \frac{pV_m[D]_0}{N}\right)^N\right][A]_0 \tag{35}$$

and again the only difference is that pV_m is substituted for V_m, compare eq 28.

Once the equilibrium constant K is determined, the absorption spectrum of the CT complexes can be obtained from eqs 29 or 35 (in the limit of large N), rewritten as

$$\epsilon_{CT}(\lambda) = \frac{\dfrac{A(\lambda)}{l[A]_0} - \epsilon_A(\lambda)e^{-K[D]_0}}{1 - e^{-K[D]_0}} = \epsilon_A(\lambda)\frac{\dfrac{A(\lambda)}{A_0(\lambda)} - e^{-K[D]_0}}{1 - e^{-K[D]_0}} \tag{36}$$

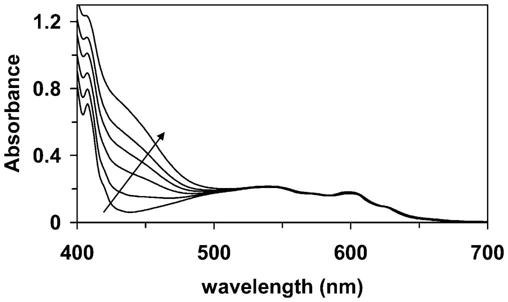

Figure 2. Absorption spectra of C_{60} + MN in toluene−MN solutions. MN concentration increases according to the arrow. The displayed curves correspond to the following MN concentrations: 0, 0.36, 1.01, 1.58, 2.16, and 3.59 M. The concentration of C_{60} is fixed at 2×10^{-4} M.

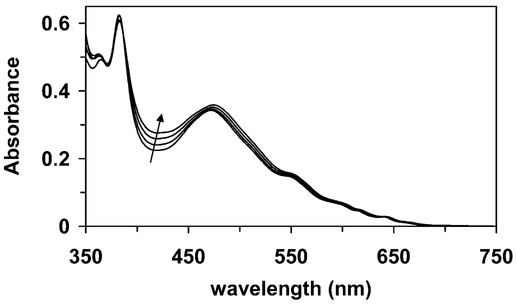

Figure 3. Absorption spectra of C_{70} + MN in toluene−MN solutions. MN concentration increases according to the arrow. The displayed curves correspond to the following MN concentrations: 0, 0.86, 2.16, and 3.59 M. The concentration of C_{70} is fixed at 2×10^{-5} M.

TABLE 1: Formation Equilibrium Constants of C_{60}−MN and C_{70}−MN in Toluene at Different Temperatures (Single DA Complex Model), Evaluated at Two Different Wavelengths

	λ (nm)		22 °C	44 °C	65 °C
C_{60}	440	K (M^{-1})	0.3	0.2	0.2
		ϵ (10^3 M^{-1} cm^{-1})	6.1	6.6	7.5
	450	K (M^{-1})	0.3	0.2	0.2
		ϵ (10^3 M^{-1} cm^{-1})	5.0	5.6	6.3
C_{70}	425	K (M^{-1})	0.1	0.1	0.1
		ϵ (10^4 M^{-1} cm^{-1})	1.9	2.1	2.1
	440	K (M^{-1})	0.1	0.08	0.1
		ϵ (10^4 M^{-1} cm^{-1})	1.9	2.0	1.8

3.4. Experimental Results. *3.4.1. Absorption Spectra.* The donor−acceptor interaction of C_{60} and C_{70} with aromatic hydrocarbons is accompanied by the appearance of at least one CT band in the 400−500-nm region of the electronic absorption spectra. Figures 2 and 3 display the absorption spectra of solutions of C_{60} and C_{70} in toluene−MN mixtures, with the CT interaction being clearly seen. Similar results are obtained in CCl_4.

3.4.2. Analysis Assuming a Single 1:1 DA Complex. Formation equilibrium constants K and CT spectra were estimated using the methods described in section 3.1. Person's criterion was fulfilled in these conditions. Data taken at different wavelengths in the spectral range of increasing absorbances were plotted according to eq 16, that is, as $[A]_0/\Delta A$ versus $1/[D]_0$. The linear regressions were used for the determination of the initial estimates of K and ϵ_{CT} that were necessary for the nonlinear fits and were performed according to eq 13. The results are summarized in Tables 1 and 2, and a typical fit is shown in Figure 4. A global error analysis was performed with all measurements, carried out at several wavelengths, and leads to the conclusion that the computed equilibrium constants

TABLE 2: Formation Equilibrium Constants of C_{60}−MN and C_{70}−MN Systems in CCl_4 at Room Temperature (Single DA Complex Model), Evaluated at Two Different Wavelengths

	C_{60}		C_{70}	
	435 nm	445 nm	410 nm	426 nm
K (M^{-1})	0.2	0.3	0.6	0.7
ϵ (10^4 M^{-1} cm^{-1})	0.85	0.65	1.9	1.9

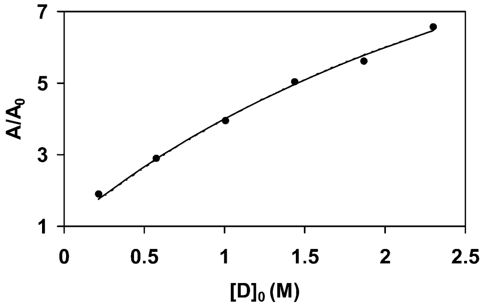

Figure 4. Reduced absorbance (A/A_0) at 440 nm of C_{60} + MN in toluene−MN solutions. MN concentration ($[D]_0$) varies from 0.2 to 2.3 M, and C_{60} concentration is fixed at 2×10^{-4} M. The solid lines corresponding to fits with eqs 13 ($K = 0.25$ M^{-1} and $\alpha = 15.9$) and 30 ($K = 0.40$ M^{-1} and $\alpha = 10.1$) are very close and cannot be distinguished in the figure.

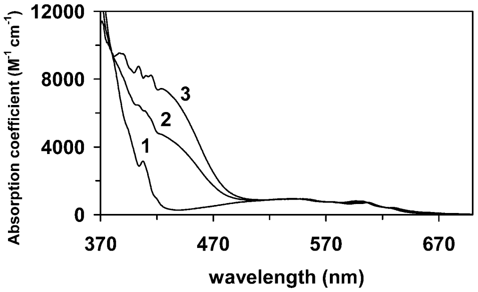

Figure 5. Absorption spectrum of the C_{60}−MN CT complex in toluene calculated according to two models: multi-equilibrium contact complexes (2) and single complex DA (3). The spectrum of C_{60} (1) is also displayed.

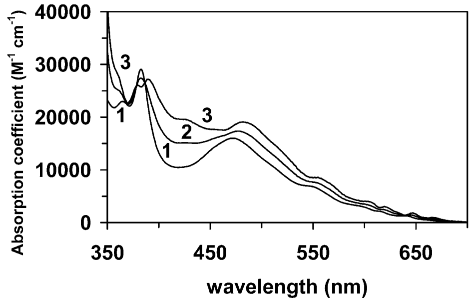

Figure 6. Absorption spectrum of the C_{70} −MN CT complex in toluene calculated according to two models: multi-equilibrium contact complexes (2) and single complex DA (3). The spectrum of C_{70} (1) is also displayed.

usually have no more than one significant figure, which suffices for our purposes.

The absorption spectra of the fullerene−MN complexes, displayed in Figures 5 and 6, were obtained from eq 18 and were found to be essentially independent of the concentration of MN. The smaller spectral changes observed for the C_{70}−MN solutions (Figure 3), compared to those of C_{60} (Figure 2), are explained by the relatively more similar spectra in the C_{70} case. The CT bands occur at similar wavelengths for C_{60} (425 nm, $\epsilon_{max} = 7400$ M^{-1} cm^{-1}) and C_{70} (424 nm, $\epsilon_{max} = 19\,600$ M^{-1} cm^{-1}). The fwhm of the bands, estimated assuming a symmetrical shape, were found to be 3700 cm^{-1} for C_{60} and 2800 cm^{-1} for C_{70}. The calculated oscillator strengths of the CT bands are $f = 0.1$ (C_{60}) and $f = 0.2$ (C_{70}), corresponding to transition dipole moments of 3 and 5 D, respectively. These values are reasonable for CT bands. Besides the CT bands, the spectra of the complexes shown in Figures 5 and 6 also display the low-energy LE bands of the fullerene. In the case of the C_{70} complex, Figure 6, the bands at wavelengths longer than 450 nm are significantly red shifted with respect to those of the free fullerene.

For a given acceptor, a linear correlation between the frequency of the CT band and the vertical ionization energy of the donor molecule is often observed,[31−33] which is also the case with fullerenes. From the analysis of a large number of C_{60} donor systems in toluene, Konarev et al.[34] obtained a good linear correlation for a broad range of ionization energies that can be rewritten as

$$\lambda_{CT} = \frac{1242}{0.90 I_p - 4.28} \tag{37}$$

where the absorption wavelength is given in nanometers and the ionization energy I_p in electronvolts. Using this correlation, the wavelength measured for the CT band of the C_{60}−MN system (425 nm) gives for 1-methylnaphthalene a vertical ionization energy of about 8.0 eV, slightly lower than that of naphthalene (8.1 eV), and in good agreement with published values.[31] For C_{70}, the measured CT wavelengths are close to those of C_{60} with the same donor, as could be expected from the similar electron affinities of the two molecules and from a previous experimental study.[34] The measured CT wavelength for the C_{70}−naphthalene complex in toluene was 421 nm ($\epsilon_{max} = 12\,000$ M^{-1} cm^{-1}). In this way, the previously reported value[25] for the C_{70}−naphthalene complex in CCl_4, 477 nm, is very likely an artifact of the method of analysis.

The estimated equilibrium constant of 0.1 M^{-1} for the C_{70}−MN system in toluene at room temperature is close to that obtained for the corresponding system with C_{60} (0.2 M^{-1}) and to those previously reported for the C_{60}−aromatic hydrocarbon systems.[20,21] Moreover, the *K* value obtained for the C_{70}−MN system in toluene is similar to that obtained for the C_{70}−naphthalene system (0.3 M^{-1}) in the same solvent. The measured molar absorption coefficients were also close to those reported[20,21] for the corresponding complexes with C_{60}.

However, the measured *K* for the C_{70}−naphthalene system (0.3 M^{-1}) is smaller than the value reported by Bhattacharya et al.[25] in room-temperature CCl_4 by 2 orders of magnitude. To check if the discrepancy was due to a solvent effect, we made measurements in CCl_4 with both fullerenes. A value of 0.6 M^{-1} was obtained for the C_{70}−MN system and a value of 0.3 M^{-1} for the C_{60}−MN system. The measured molar absorption coefficients (Table 2) were close to those obtained in toluene (Table 1). In this way, the previously reported value[25] for the equilibrium constant of the C_{70}−naphthalene complex in CCl_4, 10.6 M^{-1} at 298 K, is doubtful and is likely to, again, be an artifact of the method of analysis.

3.4.3. Analysis Assuming a Multi-Equilibrium. Considering the possibility of contact associations of the type D_nA in concentrated solutions, data were fit to eq 30. In all cases, the exponential fitting was satisfactory, as shown in Figure 4. The shape of the experimental curves of absorbance versus donor concentration (downward concavity) is not compatible with eq 32, and it can be concluded that the molar absorption coefficient

TABLE 3: Formation Equilibrium Constants K (M^{-1}) of C_{60}−MN and C_{70}−MN Complexes at Room Temperature (Multi-equilibrium Model)

toluene		CCl_4	
C_{60}	C_{70}	C_{60}	C_{70}
0.4	0.2	0.4	0.7

of the complex D_nA is not $n\epsilon_{CT}$ but is close to ϵ_{CT}, irrespective of the value of n. This is what can be expected for a low value of the orientational parameter p (see Section 3.3); even for high n, at most only one D molecule is effective in the CT interaction, and the probability of a second molecule of D in the coordinating sphere being favorably oriented at the same time being negligible. A low value of p is indeed supported by the measured K values, see Section 3.4.4 below.

The calculated spectra and equilibrium constants for the DA complex do not coincide with those previously obtained by assuming a single equilibrium. The equilibrium constants for the DA complex are slightly higher for the multi-equilibrium model (Table 3), and the absorption coefficients are correspondingly smaller. The absorption spectra of the fullerene−MN complexes, displayed in Figures 5 and 6, were obtained from eq 36 and found to be essentially independent of the concentration of MN. It is observed that they do not differ much from those obtained for the single complex model, except that the absorption coefficients are somewhat smaller. The CT bands occur at similar wavelengths for C_{60} (shoulder at 425 nm, $\epsilon_{max} = 4900\ M^{-1}\ cm^{-1}$) and C_{70} (427 nm, $\epsilon_{max} = 15\ 100\ M^{-1}\ cm^{-1}$). The fwhm of the bands, estimated assuming a symmetrical shape, were found to be 3700 cm^{-1} for C_{60} and 3300 cm^{-1} for C_{70}. The calculated oscillator strengths of the CT bands are $f = 0.1$ (C_{60}) and $f = 0.2$ (C_{70}), corresponding to transition dipole moments of 3 and 4 D, respectively.

3.4.4. Nature of the Equilibrium. The K values obtained from both models agree with the view that the complexes are of the contact type. As shown in section 3.3, one has in general $K = pV_m$; therefore, the thickness of the interaction shell cannot be estimated from eq 19 unless a value for p is assumed. The minimum thickness is obtained if $p = 1$ is used. In this case, $K = 0.1\ M^{-1}$ gives a thickness $\Delta R = 0.03$ nm, if R_c=0.71 nm is used for the fullerene−MN pair. The computed thickness is clearly too small, meaning that p is indeed much smaller than unity, as could be expected from the steric requirements of the CT $\pi-\pi$ interaction between a fullerene and a planar aromatic hydrocarbon. Quantum calculations of the CT interaction between fullerenes and aromatic donors as a function of distance and orientation would be most helpful but are not available at present.

3.4.5. Fullerene−Anthracene System. Experiments were also performed with anthracene in toluene. Only a slight increase in absorption intensity was observed for C_{70}. Owing to the very small spectral changes, no reliable K and ϵ_{CT} values could be evaluated. However, C_{60} undergoes a Diels−Alder reaction with anthracene, even at room temperature, yielding the corresponding Diels−Alder monoadduct, with characteristic absorption bands at 432 and 706 nm.[35] In this way, published results[19,22,25] on possible C_{60}−anthracene and C_{70}−anthracene CT complexes appear to be invalid.

3.4.6. Temperature Dependence. As a further, critical test on the nature of the CT complexes, we studied the effect of temperature on the equilibrium constant for the fullerene−MN systems in toluene. For both C_{60} and C_{70}, no significant changes of K with temperature were observed in the range of 22−65 °C, Table 1, in opposition to previous studies on related systems.[21,24,25] It is thus concluded that the equilibrium constant is essentially temperature independent, as expected for contact complexes.

4. Conclusions

A model for the pseudo-equilibria and absorption spectra of contact complexes was developed; in particular, it implies that a small but nonzero effective equilibrium constant can be defined for contact pairs and all higher order contact complexes. The model was applied to the study of the interaction of C_{60} and C_{70} with naphthalene, 1-methylnaphthalene, and anthracene. The results obtained (values of the equilibrium constants and absence of temperature dependence of the equilibrium constants) are explained by a contact type interaction of the fullerenes with the aromatic hydrocarbons studied.

Acknowledgment. This work was supported by Fundação para a Ciência e a Tecnologia (FCT, Portugal) within project POCTI/34400/QUI/2000. G.S. thanks the FCT for a postdoctoral grant.

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