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On the intermolecular interaction in π-exciplexes of aromatic hydrocarbons with amines

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Comparison of the energy of exciplex band maxima of aromatic hydrocarbons with dimethylaniline and diethylaniline has been used to study the nature of the intermolecular interaction in these exciplexes. For the interpretation of the results an approximate method is used to compare the zeroth-order energies of the first locally excited, LE, and charge-transfer, CT, states of the complexes. It led to the conclusion that even for strongly polar exciplexes the covalent part of the wave function can not be neglected; its weight depends on the energy gap between the first LE state and the "pure" CT state of the complex, and greatly increases when there is a near degeneracy between the first excited singlet state of the donor and acceptor molecules.

I. INTRODUCTION

Excited molecular complexes of aromatic hydrocarbons, which are unstable in the ground state, have been extensively studied since the work of Förster on the pyrene excimer[1] and that of Leonhardt and Weller on the perylene–dimethylaniline exciplex.[2]

Evidence from experimental results and comparison with excited EDA complexes proved that π exciplexes are highly polar charge-transfer complexes formed in the excited state and that the charge-transfer interaction plays a dominant role on their stability.[3-8] The energy of a "pure" charge-transfer state, $(A^- D^+)$, in the gas phase and relative to the ground state, $A + D$, can be calculated according to Eq. (1):

$$E = \mathrm{IP}(D) - \mathrm{EA}(A) - C \ , \tag{1}$$

where $\mathrm{IP}(D)$ is the ionization potential of the electron donor molecule, $\mathrm{EA}(A)$ the electron affinity of the acceptor, and C is the Coulomb energy due to the attraction between the two ions. Beens and Weller[4] and Rehm and Weller[5] have found that in cases where relatively strong acceptors are combined with relatively strong donors, the exciplex emission frequencies in n hexane are directly related to the differences of the polarographic oxidation and reduction potentials, leading to the conclusion that the energy of such complexes corresponds to a "pure" charge-transfer state, meaning that its energy is not significantly altered by mixing of the wave function with the ground state and locally excited state wave functions.

In order to contribute to the understanding of the intermolecular interaction in π exciplexes, it may prove useful to compare properties of the exciplexes of a set of aromatic hydrocarbons with two different donors. We have previously reported results taken from the fluorescence spectra of triphenylene, Tr, chrysene, Ch, pyrene, Py, anthracene, A, 1:2-benzanthracene, BA, and perylene, Pe, in dilute solutions in nonpolar solvents, with two similar donors, dimethylaniline, DMA, and diethylaniline, DEA.[9,10] Plots of the energies of the exciplex maxima against the electron affinity of the aromatic hydrocarbons, taking into account the uncertainty of their value as published in the literature, are displayed in Fig. 1. It can be seen that the linear relationship does not hold for all the molecules. In this paper we try to relate these results with the nature of the intermolecular interaction.

II. NATURE OF THE INTERACTION

The wave function of these exciplexes, ψ_c, is usually written as a mixing between charge-transfer, CT, and locally excited, LE, states:

$$\psi_c = \sum_i a_i \psi_i (DA)^* + \sum_j a_j \psi_j (D^* A) + \sum_k a_k \psi_k (D^+ A^-) \ . \tag{2}$$

Studies of transient absorption by exciplexes[11,12] confirmed the previous assumption that the contributions of the LE configurations in Eq. (3) are rather small. Consequently, in a very simple approach the wave func-
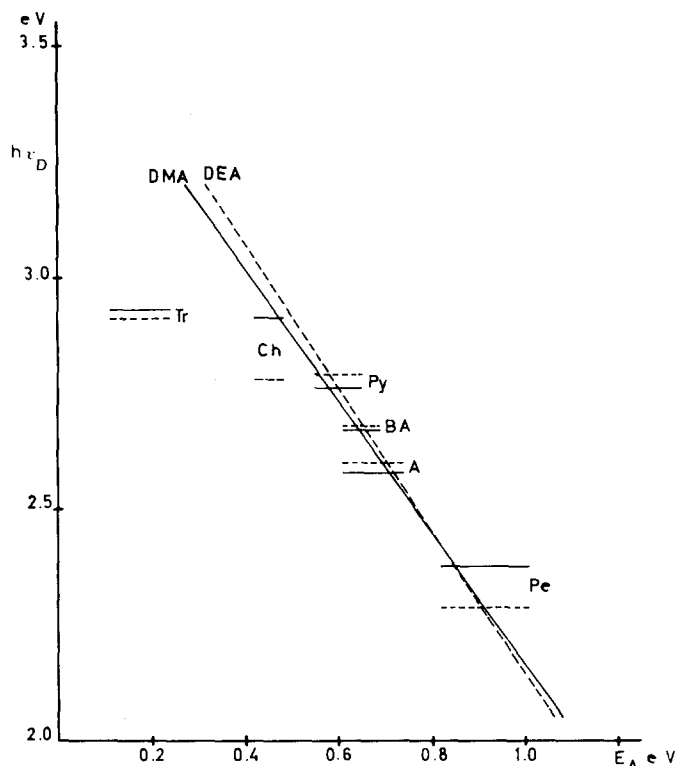

FIG. 1. Energy of exciplex band maxima plotted against electron affinity.

TABLE I. Ionization potentials, IP, and electron affinities, EA, (eV).

	Tr	Ch	Py	BA	A	Pe	Te	DMA	DEA
IP	7.95	7.7	7.55	7.47	7.45	7.15	7.0	7.14	7.0
EA	0.15	0.43	0.58	0.65	0.68	0.95	1.1	$\cdots$	$\cdots$

tion may be written in a manner analogous to that of charge-transfer complexes in Mulliken's theory[13,14]:

$$\psi_c = a\,\psi(DA^*) + b\,\psi(D^+A^-) \ . \tag{3}$$

A. Method used in the comparison of the results

As the intermolecular overlap between two π-electron systems which are 3.0–3.5 Å apart is very small, and even smaller when the size of the two molecules is very different,[15] the exchange energy is very small and most probably the same for each pair of DMA and DEA exciplexes. This fact suggests the following approximation: to neglect molecular orbital overlap and use approximate methods to determine the energies of the zeroth-order LE and CT states.

Assuming that the repulsive potential between the aromatic hydrocarbon and the aniline molecule is the same in the ground state as in the excited state,[16] the energy of the complex relative to the ground state is

$$E_{CM} = h\nu_M \quad \text{for DMA complexes}$$

and

$$E_{CE} = h\nu_E \quad \text{for DEA complexes.}$$

The effect of the solvent is not considered because it only shifts the DMA and DEA lines about 0.1 eV[15] and does not affect the comparison of the results.

The energies E_1 (the energy of the first excited state of the aromatic hydrocarbon[17]) and $E_2 = \text{IP}(D) - \text{EA}(A) - C$ represent, respectively, the energy of the $\psi(DA^*)$ and $\psi(D^+A^-)$ states. They are rough approximations from the theoretical viewpoint; however, according to Azumi, Armstrong, and McGlyn,[18] they represent initially satisfactory introduction of a somewhat correct zeroth-order energy.

B. Calculation of the energy of the charge-transfer state

The most reliable methods for the determination of ionization potentials are photoelectron spectroscopy[19–21] and the Rydberg convergence limit in the vacuum ultraviolet spectrum.[22] Nevertheless comparison with other methods may help to correct small deviations.[23–27] The values of the DMA and DEA ionization potentials were chosen keeping in mind the condition for exciplex formation[3]: $\text{IP}(A) \geqslant \text{IP}(D)$. Tetracene forms exciplex with DEA but not with DMA, then: $\text{IP}(\text{DMA}) > \text{IP}(\text{Te}) > \text{IP}(\text{DEA})$. The electron affinites were calculated with IP + EA varying between 8.10 and 8.13 eV. In Table I are listed the values of the ionization potentials and electron affinities used in the calculations.

The Coulombic attraction between the two ions formed by the transfer of one electron from one molecule to the other depends on the steric configuration of the complex. As an exciplex exists only in the excited state, its ge-

ometry is not well known, but its entropy of formation, around -18 e.u., points to a fairly rigid configuration.[28] Because it is an interaction between two π-electron systems, we might assume that the steric configuration of a π exciplex is similar to that of pyrene excimer[29] (Fig. 2) and to the α form of the perylene crystal,[30] whose fluorescence spectrum is characteristic of the perylene excimer. In both crystals the distance between the molecules is 3.5 Å. When the excimer is formed the two molecules approach. From the properties of the crystalline pyrene excimer at different temperatures, Birks and Kazzaz calculated the value 3.37 Å for the distance between the molecules.[16] Consequently, we assumed that the interplanar distance between the molecules in these exciplexes was 3.37 Å. Another point in favor of this assumption is the configuration of charge-transfer complexes in which the molecules lie parallel: the distance between the molecules is larger than 3.3 Å.[31] So the two molecules were considered parallel and oriented in such a way that the transition dipole moments for the first excited state were parallel. This configuration increases a possible dipole–dipole interaction between the molecules, and the calculations showed that it corresponds to a larger value of C and then to a higher stability for the complex (Figs. 2–3).

To calculate the Coulombic interaction C we consider only the highest occupied $(1,1')$ and the lowest vacant $(2,2')$ molecular orbitals of the donor and acceptor, respectively, and assume that the more tightly bound molecular orbitals are not significantly changed by the formation of the exciplex. This approximation has been used for excimers.[18,32] Then C may be expressed as

$$C = (11 \,|\, 2'2') = \sum_\mu \sum_\nu C_{\mu1}^2 C_{\nu2'}^2 \cdot (\mu\mu \,|\, \nu\nu) \ , \tag{4}$$

where $C_{\mu1}$ and $C_{\nu2'}$ are the coefficients of the LCAO expansion of the molecular orbitals and $(\mu\mu \,|\, \nu\nu)$ are the intermolecular Coulomb repulsion integrals.

For aniline, pyrene, anthracene, and perylene the values of the LCAO coefficients were calculated with a Pariser–Parr–Pople program. For triphenylene, chrysene, and 1:2-benzanthracene, as this program failed to converge, HMO coefficients were used and it was assumed that the deviation of C_{HMO} relatively to C_{PPP} is not larger than 0.05 eV.

According to Azumi, Armstrong, and McGlynn,[18] and Lami and Laustriat,[33] the intermolecular Coulomb repulsion integrals can be calculated by the multipole expansion method proposed by Parr,[34] applied to two parallel π-electron systems:

$$(\mu\mu \,|\, \nu\nu) = e^2 \left\{ \frac{1}{R} + \frac{1}{4R^3} \left[(q_\mu + q_\nu)(3\cos^2\theta - 1) \right] \right.$$
$$\left. + \frac{3q_\mu q_\nu}{16R^5} (3 - 30\cos^2\theta + 35\cos^4\theta) \right\} \ ,$$

FIG. 2. Steric configurations.

TABLE III. Energy levels E_1, E_2, and E_C (eV).

	Tr	Ch	Py	BA	A	Pe
E_1	3.62	3.41	3.35	3.20	3.27	2.84
E_2 (DMA)	3.64	3.42	3.28	3.16	3.08	3.00
E_2 (DEA)	3.50	3.28	3.14	3.02	2.94	2.86
E_{CM}	2.93	2.91	2.76	2.67	2.58	2.38
E_{CE}	2.91	2.78	2.79	2.68	2.60	2.29

electron from DMA or DEA to these aromatic hydrocarbons, as it has been suggested by Beens and Weller[4] and Rehm and Weller,[5] and is verified for charge-transfer complexes with chloranil. It may be concluded that the the weight of the term $\psi(DA^*)$ on the total wave function is more important than has been suggested by some experiments of exciplex absorption.[12]

(b) For both DMA and DEA, the triphenylene exciplex energy lies well below the line. Because the value of C is nearly the same as for the other molecules, this result can only be explained by further stabilization of the
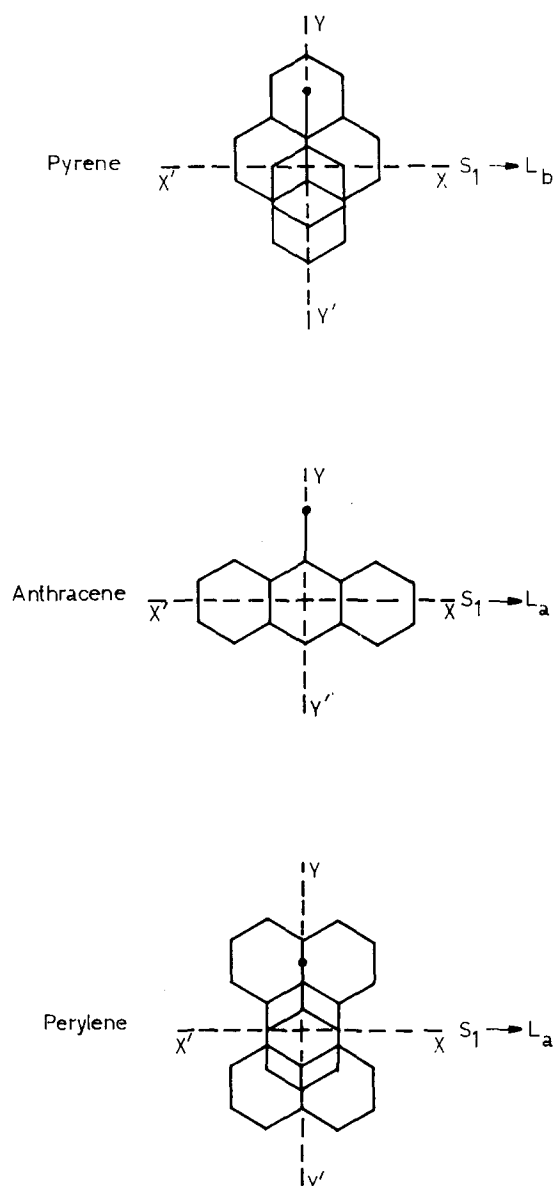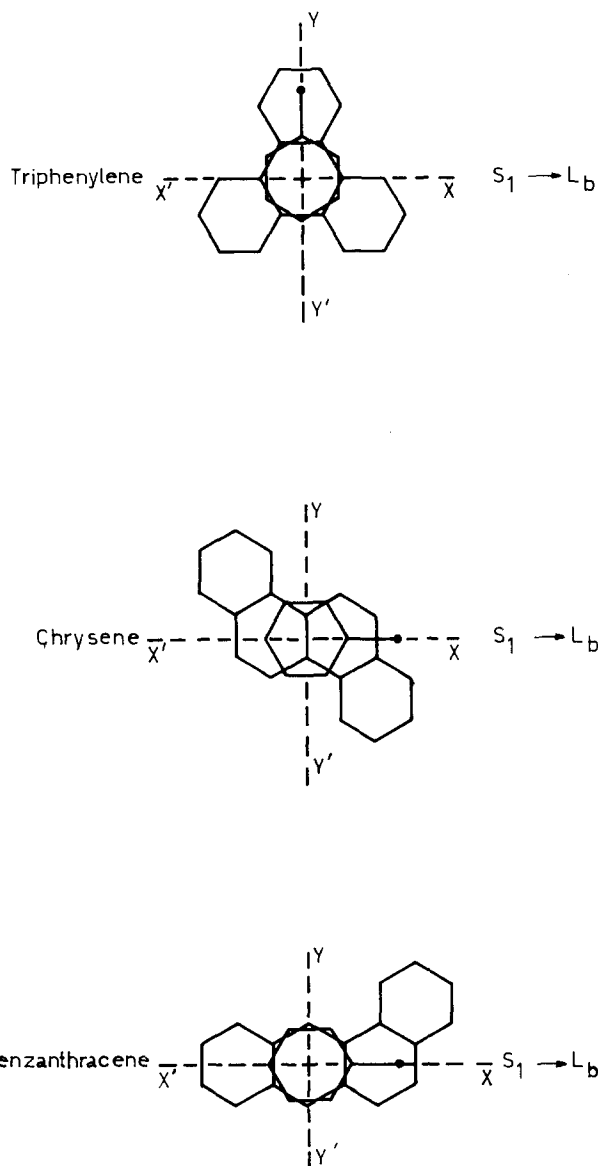
where $\cos\theta = d/R$; R is the distance between the centers of the p orbitals; d the distance between the molecules; and $q = 24 a_0^2/Z^2$, a_0 being the Bohr radius.

In Table II are listed the values of C used in the calculation of the zeroth-order charge-transfer state energy, E_2, and in Table III the values of E_1, E_2, and E_c.

III. DISCUSSION

(a) In Fig. 1 the slope of the straight lines is not -1, suggesting that there is not a complete transfer of one

TABLE II. Coulomb attraction energy between the positive and negative ions, C (eV).

d (Å)	Tr (HMO)	Ch (HMO)	Py (PPP)	BA (HMO)	A (PPP)	Pe (PPP)
3.37	3.30	3.29	3.28	3.33	3.38	3.19

FIG. 3. Steric configurations.

Chrysene

E_2, E_1,]0.01, |0.50, |0.51, E_c, $h\nu_M$ = 2.91, E_0

E_1, |0.13, E_2, 0.63, |0.50, E_c, $h\nu_E$ = 2.78, E_0

Perylene

E_2, E_1, ‡0.16, |0.46, |0.62, E_c, $h\nu_M$ = 2.38, E_0

E_2, E_1,]0.02, |0.5ᶜ, |0.57, E_c, $h\nu_E$ = 2.29, E_0
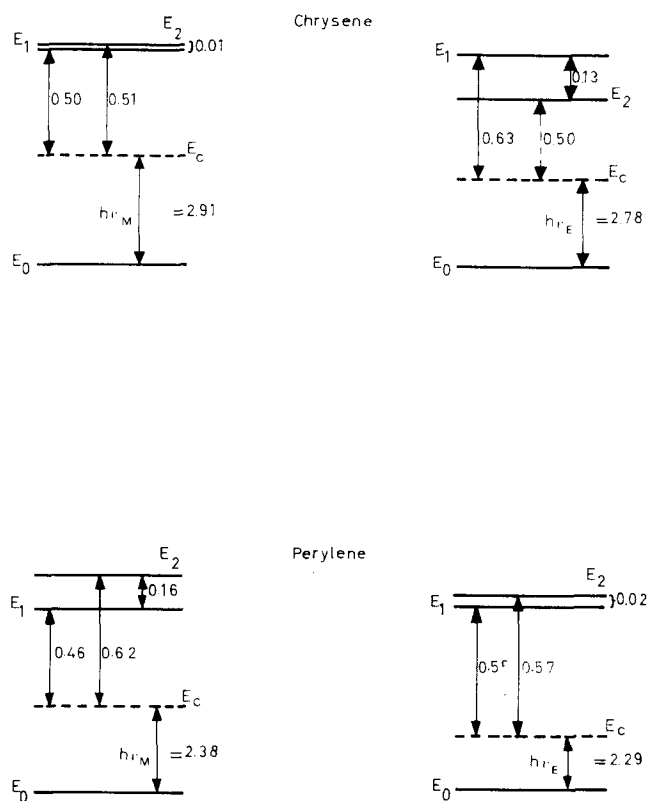
FIG. 4. Comparison of energy levels for chrysene and pery-lene.

complex by an exciton molecular interaction. In fact, of all the molecules studied, triphenylene is the only one whose fluorescence spectrum has a small "overlap" with the DMA absorption spectrum, meaning that a photon emitted by triphenylene can be absorbed by DMA and *vice verse*. In this case there is an accidental degeneracy of the states $\psi(DA^*)$ and $\psi(D^*A)$ and Eq. (3) can not represent, not even roughly, the wave function of these exciplexes. So in this case the first term, $\psi(DA^*)$, has to be replaced by a linear combination of $\psi(D^*A)$ and $\psi(DA^*)$, according to the perturbation theory for the generate states.

As the absorption spectrum of DEA is shifted to the red relatively to that of DMA, a dipole–dipole interaction becomes possible also for excited chrysene and DEA: the position of the Ch–DEA exciplex relatively to the DEA line shows that this additional interaction comes into play.

(c) The perylene–DMA exciplex is a little above the line: this position is due not only to a smaller value of C (because Pe–DEA fits better into the DEA line), but also to a smaller interaction between the two states $\psi(DA^*)$ and $\psi(D^*A^-)$ due to the large energy gap $E_2 - E_1$ (Fig. 4). With DEA there is an increase in the interaction: unlike the chrysene exciplex a dipole–dipole interaction is not probable here, the increased interaction being due to a decrease in the energy gap $E_2 - E_1$. Note that for chrysene there is an *increase* in the interaction with DEA instead of a *decrease* to be expected from the larger value of $E_1 - E_2$ (Fig. 4).

(d) For anthracene there is a smaller mixing of the

two states due to the higher value of $E_1 - E_2$, but it is compensated by a higher value of C, and consequently anthracene fits approximately on the DMA and DEA lines. Anthracene shows the highest value of C. It is the only one of these hydrocarbons that forms photo-dimers.

(e) While IP(DEA) < IP(DMA), it would be expected from Eq. (1) that $h\nu_E < h\nu_M$, as it has been verified by Itoh[35] and Rehm and Weller[5] and is a usual behavior for EDA complex interactions. This is not so for these exciplexes of pyrene, anthracene, and 1:2-benzanthracene, for which $h\nu_E > h\nu_M$. This result must be due to the relative position of the energy levels E_1 and E_2. For DEA, $(E_1 - E_2)$ increases and the interaction decreases. The decrease in the interaction term is not compensated by a decrease in E_2 and so $(E_1 - E_c)$ for DMA is larger than $(E_1 - E_c)$ for DEA. The hypothesis previously suggested[10] to explain this result, assuming a steric effect due to the ethyl group, is not necessary. Similarly, the energy of the exciplexes should decrease when increases the electron affinity of the acceptor. This is so for the series of DMA exciplexes but not for the DEA exciplexes, as $h\nu_E(\text{Ch}) < h\nu_E(\text{Py})$. This fact again stresses the increased interaction in the Ch–DEA exciplex.

IV. CONCLUSION

Comparison of the energy of the exciplexes formed by pyrene, triphenylene, chrysene, anthracene, perylene and 1:2-benzanthracene with DMA and DEA show that even for strongly polar exciplexes the covalent part of the wave function ψ_c can not be neglected in the calculation of the state energy. Its weight on the total wave function depends on the energy gap between the first LE state and the "pure" CT state of the complex, and greatly increases when there is a near degeneracy between the first excited singlet state of the donor and acceptor molecules, envolving then the first excited state of both molecules.

ACKNOWLEDGMENTS

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