PHOTOPHYSICS OF WEAKLY INTERACTING

MOLECULAR SYSTEMS

Ву

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ABSTRACT

PHOTOPHYSICS OF WEAKLY INTERACTING MOLECULAR SYSTEMS

By

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Molecular systems in which the molecules are far apart such that intermolecular interactions are negligibly small are considered as free, i.e., isolated molecular systems. The studies of such systems are of great significance since they provide us with basic information regarding the nature of electronic states and emission characteristics of single molecules.

If weak interaction occurs between molecular components forming the system, the excitation of the assembly as a whole should be considered rather than isolated molecules. Interactions in composite systems may be too weak to cause a significant change in the absorption properties of the corresponding isolated molecular system yet strong enough to cause a variety of phenomena such as: excitation delocalization, proton transfer, excimer and exciplex formation leading to significant alternations in the luminescence properties of the system.

This work reports on the luminescence properties of two weakly interacting molecular systems: α -carboline

hydrogen bonded dimer and its acetic acid complex and 1,3diphenyl propane derivatives, ϕ -CH₂-X-CH₂- ϕ , in which X is -CH₂-, - \ddot{O} -, - \ddot{N} - or -S-.

In the a-carboline system, a long wavelength fluorescence band has been characterized as the emission of a tautomer which is formed in the excited state of α -carboline as a result of a double proton transfer process. The dynamics and energetics of this process has been studied by examining the luminscence properties of the system under various conditions. Both steady state and nanosecond timeresolved emission techniques were used in this study. The rate constants of the proton transfer process in deuterated α -carboline at 77°K are $K_f = 6.7 \times 10^7 \text{ sec}^{-1}$, $K_b =$ 2.1 x 10^7 sec⁻¹. The energy barrier for the forward process is estimated to be 2.95 Kcal/mole. Proton tunneling contributes to the transfer process and becomes the only mechanism of transfer at low temperature.

For the α -carboline-acetic acid complex, a forward rate constant of 8.9 x 10⁸ sec⁻¹ was obtained and the energy barrier is estimated to be 0.18 Kcal/mole. Both α -carboline and acetic acids protons were replaced by deuterium. The biological relevance of double proton transfer in DNA base pairs is discussed briefly.

In the second system, the heteroatom acts as an electron doner with respect to the benzene ring leading to charge transfer interaction. This implies that in the ground state conformations that allow overlap of the lone pair orbital with the benzene p_i orbitals are relatively stable. This charge transfer interaction manifests itself in the absorption spectra by intensity enhancement that is consistent with the ionization potential of the heteroatom. The fluorescence spectra of these compounds are solventdependent. In hydrocarbon solvents, one observes excimer emission corresponding to a sandwich-type conformation where the two benzene rings are parallel. Such emission occurs at 340 nm and its energy is essentially independent on the heteroatom. The fluorescence intensity decreases as the ionization potential of the heteroatom decreases. In polar solvents, a unique solvent-induced emission is observed, that shifts to larger wavelength as the polarity of the solvent is increased. In very polar solvents (water) the emission is very weak. Such emission originates from an exciplex which is stabilized by dipole-dipole interaction with the solvent. The configuration of such exciplex is a "butterfly" conformation that allow overlap of the lone pair orbitals with the \boldsymbol{p}_i orbitals of the aromatic moiety. Moreover, triplet excimer emission has been identified in these compounds.

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CHAPTER I

PHOTOPHYSICS OF WEAKLY INTERACTING MOLECULAR SYSTEMS

A. Introduction

Phenomena associated with electronic excitations of molecular systems may be classified into various categories depending on the extent of <u>intermolecular interaction</u> in the system the <u>number of radiative steps</u> involved in the excitation process and whether <u>linear or non-linear</u> excitation (a single vs. a multiple photon process) is involved.

1. Single Molecule vs. Composite Molecular Systems:

Molecular systems in which the molecules are far apart such that intermolecular interactions are negligibly small are considered as <u>free or isolated molecular systems</u>. Examples include: gas phase systems at reduced pressures, very dilute solutions of aromatic systems in inert solvents and dilute mixed crystals. In the latter two cases solutesolvent interactions are neglected since the solvent used is such that its low-lying electronic states are much higher in energy than that of the solute.

On the other hand, if weak interaction occurs between the molecules forming the system, the excitation of the

assembly as a whole, i.e., the composite system^{1,2,3} rather than a single molecule excitation must be considered. Intermolecular interaction may be weak such that only small overlap occurs between neighboring molecules and therefore their state wavefunctions are approximately orthogonal. The optical properties of the composite system are determined basically (in the zeroth order) by the optical properties of the free molecule, the influence of intermolecular interaction being treated as a perturbation. Examples of molecular composite systems include condensed phase systems such as gases under moderate or high pressures, liquids, aggregates (polymers) and crystals (pure and mixed). Concentrated solutions where the average intermolecular distance is small or where dimerization or complex formations may take place are composite systems of common occurrence. Polyatomic molecules with covalently bonded molecular units may also be considered as composite systems. Although intermolecular interactions in composite systems are weak, unique excitation phenomena are observed.

2. One Step Versus Two Step Excitations

Excitation of a certain electronic state may take place in one or two distinct radiative steps in this latter case an intermediate metastable state (e.g., triplet state) may be involved. We count only radiative primary steps in which energy of the field and the molecular systems is

conserved.

3. Single Photon Versus Multiphoton Processes

Under usual conditions the pertubation of the molecular systems by the electromagnetic field of light is small such that only terms linear in the vector potential are considered, leading to the creation or destruction of one photon in the field namely single-photon processes. However, at high photon flux (as in lasers) second-order terms in the vector potential become important.^{4,5,6} Such terms involve the creation or destruction of more than onephoton in the field leading to two-photon (non-linear) absorption.

Many studies have been concerned with, <u>Single-Photon</u>, <u>Single-Molecule processes</u> in which the free molecule is perturbed by the linear terms of the radiation field only, electrostatic fields due to other molecules being completely neglected. Although such ideal systems may not be common in nature the optical properties of composite systems which are of more common physical occurrence are basically determined by the optical properties of the free molecule. Careful spectroscopic studies involve an examination of the absorption and luminescence spectra under various conditions and the use of perturbation experiments (solvent effects, paramagnetic and heavy atom effects, temperature effects, steric effects, substitution effects, pH effects, external field effects). Such careful studies

give information regarding the multiplicity (S vs. T), symmetry, orbital promotion type (e.g., $n+\pi^*$ vs. $\pi+\pi^*$), polarization, sequence and spacing, and chemical reactivity of the lowest electronic states (pk_a , pk_b , hydrogen bonding ability, etc.). The absorption properties (oscillator strength, vibrational modes coupled with the various excited electronic states, potential energy functions, etc.) and the emission properties (fluorescence and phosphorescence quantum yields, life-times, etc.) are also deduced from such measurements. Answers to such basic questions as the detailed paths of electronic excitations, correlation of photochemical reactivity with the spectroscopic properties of the electronic states and radiationless transition mechanism are sought and hopefully answered by such studies.

Single-photon Composite System processes

Both the radiation field and the electrostatic field of neighboring molecules must be considered in order to account for the numerous phenomena associated with electronic excitation of composite systems. Interaction in a composite system may be so weak as to cause a negligible change in the absorption properties yet strong enough to cause a variety of emission related phenomena, such as excitation delocalization (excitons), excited state proton transfer, charge transfer, energy transfer, molecular excimers, and exciplexes. Significant changes

in the luminescence properties of a molecule are often associated with the occurrence of such phenomena.

This research is primarily concerned with the role that intermolecular interactions play in two molecular systems.

The first system is a-carboline (l-azacarbazole) which ixhibits excited state double proton transfer in its hydrogen bonded dimer and its acetic acid complex. The study of the dynamics and energetics of the proton transfer process in such systems constitutes one main research goal. Results and discussion of this section are presented in Chapter II.

The second molecular system comprise diphenyl propane derivatives of the type ϕ - CH₂ - X - CH₂ - ϕ . Where X = -CH₂-, - $\overset{"}{O}$ -, - $\overset{"}{N}$ -, - $\overset{"}{S}$ -. These molecules exhibit intramolecular charge transfer as well as singlet and triplet excimer interactions. The examination of various possible types of interactions charge transfer, excimer and exciplex interactions has been the focus of this portion of the study. The results and discussion are presented in Chapter III. The related molecular system ϕ -CH₂- $\overset{"}{H}$ -CH₃ exhibits solvent induced exciplex emission.

A summary of the literature background on excited state proton transfer, charge transfer, excimer and exciplex interaction is presented in Chapter I. The experimental technique used in this research is contained in Chapter 5. A brief discussion of possible biological

applications is given in Chapter IV.

B. Excited State Proton Transfer

1. Proton Transfer

The phenomenon of proton transfer in the ground state is called "tautomerism." Both the enol form and the keto forms may exist in the same solution, with the equilibrium thermally controlled. Similarly proton transfer may occur in the excited state and is called "phototautomerism." Since the electron density distribution in the excited state may be very different from that of the ground state, the proton will transfer from one position to another more protonphilic position. The emission from this excited tautomer may be shifted with respect to that of the original species. The relative intensities of these two emission bands depends on the efficiency of the proton transfer process and the quantum yields of the original molecule and its tautomer.

Proton transfer may occur intramolecularly as in salicylic^{7,8,9} acid or intermolecularly as in the 7-azaindole hydrogen bonded dimer.^{10,11}

The study of absorption and emission spectra as a function of pH is very useful in determining the pk value of the excited state. The β -naphthol case will be used as an example to illustrate how the excited singlet state dissociation constant pk may be calculated. If the proton transfer occurs in the excited state and not in the ground

state, the value of ΔH^* must be less than that of ΔH . The schematic diagrams shown below represents the thermochemistry of proton transfer reaction in the ground and first excited singlet state.



Figure 1

From the diagram, one can write the following relations:

 $\Delta E_1 + \Delta H^* = \Delta E_2 + \Delta H$ $\Delta H^* - \Delta H = \Delta E_1 - \Delta E_2$

It is reasonable to assume that $\Delta S^* = \Delta S$, i.e., entropy changes associated with the proton transfer process are same whether it occurs in the ground state or in the excited state.

The difference of free energy between the excited state and the ground state can be written as:

$$\Delta G^{*} - \Delta G = (\Delta H^{*} - \Delta H) - T(\Delta S^{*} - \Delta S)$$
$$= \Delta H^{*} - \Delta H$$

using the relation between ΔG and the equilibrium constant K

 $\Delta G = -RT \ln Keq$

-2.303 RT (log K^{*}/K) =
$$\Delta H^* - \Delta H = \Delta E_1 - \Delta E_2$$

(pk^{*} - pk) = $\frac{\Delta E_1 - \Delta E_2}{2.303 \text{ RT}}$

To determine the ΔE values from the spectrum, one can obtain the ΔE value from either absorption or emission data, or from the mean of the absorption and emission.^{12,13,14} However, such values may be measured using the 0 - 0 bands or the maxima of absorption or emission bands. By assuming that the spacing between the vibronic levels in the ground state and the excited state is the same in both protonated and deprotonated species,^{15,16} the energy difference between the 0 - 0 band will be the same as the energy difference between the maximum of absorption or emission.

 $(v_{00}^{\text{HA}} - v_{00}^{\text{A}})$ abs or emission = $(v_{\text{max}}^{\text{HA}} - v_{\text{max}}^{\text{A}})$ abs. or emission

HA is the protonated species A is the deprotonated species

In most cases, the "maximum" way has been used because the 0 - 0 band is difficult to determine because of the broad spectra of the solute molecule and the solventsolute interactions. Equation can be written as follows

$$pk_{a}^{*} - pk_{a} = \frac{Nh}{2.303 \text{ RT}} \quad (v_{max}^{HA} - v_{max}^{A})$$

N = Avogadro's constant

h = Planck's constant

2. Proton Tunneling

In fact, the thermal energy of proton is not enough to overcome the energy barrier, but the proton has been found in the other side of barrier. It can be explained in terms of tunneling effect of wave mechanics.

Two kinds of potential barrier have been assumed for studying and explaining the proton transfer. The first is the Eckart barrier which although similar to the real potential barrier has some disadvantages;^{17,18} the derivation of the probability is much more complicated. The barrier function is as follows:

 $V(X) = \{A \exp (2\pi x/\ell)\} / \{1 + \exp (2\pi x/\ell)\} +$

 $\{B \exp (2\pi x/\ell)\} / \{1 + \exp (2\pi x/\ell)\}^2$

x is the cartesian coordinate, and A, B, and 1 are constants. The graphs of this function for various values of A and B are shown in Figure 2. It approach zero for large negative values of x and a constant value A for large positive values. The width of the transition region is, practically speaking, 21.

For the large positive values of X, corresponding to completion of the proton transfer, the single transmit $t \in d$



Fig. 2. Graphs of the function V(x). The numbers on the curves are the values of B/A.

•

wave:

$$\psi$$
 = a exp (2 π ix/ λ ')

where

$$\lambda' = \frac{h}{2m(w-A)^{\frac{1}{2}}}$$

For a large negative value of X, the solution will be in two parts. One is incidental and the other is reflected, corresponding to the proton approaching the barrier and those not transmitted.

$$\psi = a_1 \exp (2\pi i x/\lambda) + a_2 \exp (-2\pi i x/\lambda)$$

where

$$\lambda = \frac{h}{(2mw)^{\frac{1}{2}}}$$

The quantity $\rho = (a_2/a_1)^2$ may be called the reflection coefficient; the transmission coefficient or permeability G of the barrier is $(1-\rho)$. These may be expressed in terms of the barrier parameters A, B, and 1 and the energy w of the incident particle. The equation is

$$\rho = |a_2/a_1|^2$$

$$= \left| \frac{\Gamma(\frac{1}{2} + i(\delta - \beta - \alpha)) \Gamma(\frac{1}{2} + i(-\delta - \beta - \alpha))}{\Gamma(\frac{1}{2} + i(\delta - \beta + \alpha)) \Gamma(\frac{1}{2} + i(-\delta - \beta + \alpha))} \right|^{2}$$

where $\alpha = 1/\lambda$; $\beta = 1/\lambda'$; $C = h^2/8ml^2$; $\delta = \frac{1}{2}[(B-C)/C]^{\frac{1}{2}}$

If the barrier is not too narrow B > C, then the permeability
"G" of proton with energy w will be

$$G = 1 - \rho$$
$$= \frac{\cosh \{2\pi(\alpha+\beta)\} - \cosh \{2\pi(\alpha-\beta)\}}{\cosh \{2\pi(\alpha-\beta)\} + \cosh (2\pi\delta)}$$

The plot of G with respect to w/E, E is the height of energy barrier, shows positive value even w/E is less than 1, which indicated proton tunneling.

The second type of barrier is the parabolic barrier.^{19,20}

$$V(x) = E(1-x^2/a^2)$$

a is the one half of parabolic width, E is the height of energy barrier. It is easier for derivation of G value but the results isn't good.

C. Excimers-Exciplexes-Charge Transfer Complexes

In 1954 Forster and $Kasper^{21}$ were studying the concentration dependence of pyrene fluorescence when they observed that by increasing the concentration of pyrene, the fluorescence emission band $(0, 0 \sim 27,000 \text{ cm}^{-1})$ was quenched, while a new broad and structureless emission started appearing with a peak intensity red shifted by $\sim 6000 \text{ cm}^{-1}$. The authors ascribed this new emission to an excited state association between two pyrene molecules. For several years this behavior was considered somehow unique to pyrene. Birks²² showed the phenomenon is common to most aromatic hydrocarbons and their derivatives.

Excited state associations between different kind of molecules are called "exciplexes." They were discovered by Leonhardt and Weller²³ in 1963, where it was found that upon quenching the fluorescence of aromatic hydrocarbons by aromatic amines, like anilines, a new broad band appeared about 5000 cm⁻¹ to the red of the hydrocarbon emission. This emission was assigned to an excited complex of the hydrocarbon and the amine. Exciplexes between simple atomic systems like (KrAr)^{*} were also reported recently.²⁴

The observation of a broad structureless emission band is not the only manifestation of excimer formation. There are several criteria from which we mention the following:

(1) The appearance of the broad emission band is not associated with any changes in the absorption spectra. Even after prolonged irradiation no change is detected in the absorption spectrum. This supports the idea that the new emission is not due to photoproducts.

(2) The emission spectra show an "isostilbic" point indicative of the excited state equilibrium.

(3) From Stern-Volmer relations the ratio of fluorescence intensities of the dimer and monomer is expected to be proportional to monomer concentration; this is actually observed. No concentration-dependent changes are observed

in the absorption spectrum.

(4) The excimer formation is viscosity dependent and shows the characteristics of diffusion controlled reactions.

(5) The decay of the monomer is usually described by a single exponential. If the excimer dissocation rate is significant then the monomer decay is described by a sum of two exponentials. Finally if equilibrium is established in the excited state then both monomer and excimer will decay with a common lifetime.

(6) Thermodynamic data always yield negative entropy changes characteristic of association processes. Several other results point to an excited state reversible association and we will talk about them next.

Excimer formation is not unique to fluid phases but is common in molecular crystals. Stevens²⁵ proposed a general relationship between fluorescence and crystal structure of aromatic compounds. "Elongated" molecules like naphthalene, anthracene, phenanthrene, favor structures of an A type, in which adjacent molecules are oriented almost perpendicular to one another. "Disk-Shaped" molecules on the other hand, favor structures of a B type, in which the molecules are either arranged in pairs (pyrene, benzo(g,h,i) perylene, a-perylene) or stacked in columns (B-perylene, coronene, ovalene). Excimer fluorescence occurs only in crystals of the B type. The absorption spectra do not show any strong interactions

(slight Davydow splitting may be observed). In the crystal, further relaxation is needed from the ground state arrangement for excimer formation to occur. Thus α -perylene no longer exhibits excimer fluorescence at very low temperatures, ²⁶ while crystals of type A under pressures of 10-50 kbar show partially excimeric emission.²⁷ Polymers like polystyrene and polyvinylnaphthalene exhibit excimeric emission.²⁸

Excimers and exciplexes can be formed in a variety of other situations, for example:

- a. Radical ion annihilations (Chemiluminescence) $A^- + A^+ \longrightarrow (AA)^*$
- b. Triplet-Triplet annihilation ${}^{3}A^{*} + {}^{3}A^{*} \longrightarrow {}^{1}(AA)^{*}$

c. Photodecomposition of dimers, like dianthracene. The literature on excimers has been reviewed extensively by Forster,²⁹ Birks³⁰ and Stevens.³¹

While experimentally the phenomenon of excimer association appears well established, the theoretical description of the phenomenon is not complete. The most commonly used description of the excimer state is as a mixture of "exciton resonance and charge-transfer states." In the following the molecular exciton and the charge-transfer models will be discussed together with a model which considers both exciton and charge-transfer interactions. Since excimer luminescence reflects both excited and ground state interactions, the forces present in both cases will be discussed.

1. Excited State Interaction - The Molecular Exciton Model

The exciton concept was introduced into solid state physics by Frenkel in 1931³² in connection with the transformation of excitation energy into heat in raregase solids. In 1948 A.S. Davydow³³ applied the molecular exciton model to the problem of the electronic states of naphthalene crystals. Since that time and especially after the publication of Davydov's book "Theory of Molecular Excitons,"³⁴ a great variety of problems in the area of molecular and solid state physics have been approached theoretically using exciton theory. For a recent review of the exciton theory and its applications see the article by Philpott.³⁵ Here we are going to consider in the most simplified form the interaction of an excited and an unexcited molecule on the basis of the exciton model. Suppose we have two molecules A and B (of the same kind) in proximity. Now we consider that molecule A absorbs a photon and becomes excited, then we can write the wavefunction of the system as

$$\psi_1 = \phi_a^* \phi_b$$

On the other hand if the excitation is localized on b the wavefunction will be

$$\psi_2 = \phi_a \phi_b^*$$

 ψ_1 and ψ_2 are degenerate states and do not describe stationary states of the system. Proper linear combinations of these two localized states are stationary states of the dimer. This is a simple case of degenerate perturbation theory. The first order energies can be found from the determinant:

$$\begin{array}{ccc} H_{aa} - E & H_{ab} \\ & & & \\ & & & \\ H_{ab} & H_{bb} - E \end{array} = 0$$

where

$$H_{aa} = H_{bb} = \langle \phi_a^* \phi_b | H | \phi_a^* \phi_b \rangle$$
$$H_{ab} = H_{ba} = \langle \phi_a^* \phi_b | H | \phi_a \phi_b^* \rangle$$

(* denotes electronic excitation, not complex conjugates), the roots of the determinant are

$$E' = H_{aa} + H_{ab}$$
$$E'' = H_{aa} - H_{ab}$$

and the eigenvectors

$$\psi' = 2^{-\frac{1}{2}} (\phi_a^{*} \phi_b + \phi_a \phi_b^{*})$$

$$\psi'' = 2^{-\frac{1}{2}} (\phi_a^{*} \phi_b - \phi_a \phi_b^{*})$$

In both stationary exciton states ψ' and ψ'' the excitation is on both molecules, A and B, i.e., the excitation is collective or delocalized. The node corresponding to the minus sign in the exciton wavefunction is an excitation node. At the excitation node, the phase relation between transition moments on the respective molecular centers changes sign.

Evaluating E' and E" we get:

$$E^{*} = E_{a}^{*} + E_{b} + \langle \phi_{a}^{*} \phi_{b} | V_{ab} | \phi_{a}^{*} \phi_{b} \rangle + \langle \phi_{a}^{*} \phi_{b} | V_{ab} | \phi_{a} \phi_{b}^{*} \rangle$$

$$E^{*} = E_{a}^{*} + E_{b} + \langle \phi_{a}^{*} \phi_{b} | V_{ab} | \phi_{a}^{*} \phi_{b} \rangle - \langle \phi_{a}^{*} \phi_{b} | V_{ab} | \phi_{a} \phi_{b}^{*} \rangle$$

the term $\langle \phi_a^* \phi_b | V_{ab} | \phi_a^* \phi_b \rangle$ represents again the van der Waals forces and almost always results in a lowering of the energy of the system. If there are energy levels between the two states involved in the photon resonance and the ground state then a situation may arise that this terms leads to repulsion. In the ground state van der Waals forces are always attractive. The last term in these equations is the "exciton splitting"

$$\Delta \varepsilon = \langle \phi_{\mathbf{a}}^{*} \phi_{\mathbf{b}} | \mathbf{v}_{\mathbf{a}\mathbf{b}} | \phi_{\mathbf{a}} \phi_{\mathbf{b}}^{*} \rangle$$

It represents the effect of photon exchange between A and B. Again using the dipole approximation for V_{ab} and recognizing that

 $\langle \phi_a | X_a | \phi_a^* \rangle = M_a^X : x \text{ component of the transition}$ moment of A

 $\langle \phi_b | X_b | \phi_b^* \rangle = M_b^X$: x component of the transition moment of B, etc.,

the exciton splitting term is given by the general expression

$$\Delta \varepsilon = -|\mathbf{M}_{a}|^{2} / \mathbf{R}_{ab}^{3} (2\cos \theta_{b}^{z} - \cos \theta_{b}^{z} - \cos \theta_{a}^{y} \cos \theta_{b}^{y}$$
$$-\cos \theta_{a}^{x} \cos \theta_{b}^{x})$$

where M_a represents the transition moment in the free molecule, and $\cos \theta_a^X$, $\cos \theta_a^Y$, $\cos \theta_a^Z$ represent the cosines of the angles which the transition moment of a, M_a makes with the x, y, z axes of the coordinate frame. The maximum exciton interaction will appear when the two molecules are stacked in a perfect way, "perfect sandwich" configuration. The exciton splitting will be given then by

$$\Delta \varepsilon = -M_a^2/R_{ab}^3$$

Experimentally M is obtained from the absorption of a dilute solution of the compound under consideration using the equation

$$M^2 = 3.97 \times 10^{-20} e^2 f e d \overline{v} / \overline{v}$$

ε is the molar extinction coefficient and e is the electronic charge in e.s.u. Figure 28 describes the case of a "perfect sandwich" dimer. Although in the molecular dimer two exciton states theoretically result from the exciton splitting, both of these may not necessarily be observed as allowed spectral transitions. Let us examine the spectral selection rules by evaluating the matrix elements of the electric diple operator between the ground state and the stationary exciton states of the dimer. Thus, the transition moment vector of the dimer is given by

$$\mathbf{M'} = \langle \psi_{\mathbf{G}} | \mathbf{M}_{\mathbf{a}} + \mathbf{M}_{\mathbf{b}} | \psi' \rangle$$

$$\mathbf{M}^{\mathbf{"}} = \langle \psi \mathbf{G} | \mathbf{M}_{\mathbf{a}} + \mathbf{M}_{\mathbf{b}} | \psi^{\mathbf{"}} \rangle$$

or M', M" =
$$[\langle \phi_a \phi_b | M_a + M_b | (\phi_a^* \phi_b \pm \phi_a \phi_b^*) \rangle] / 2^{\frac{1}{2}}$$

Orthogonality and normalization properties of the wavefunctions lead to:

$$M' = \langle \phi_{a} | M_{a} | \phi_{a}^{*} \rangle / 2^{\frac{1}{2}} + \langle \phi_{b} | M_{b} | \phi_{b}^{*} \rangle / 2^{\frac{1}{2}}$$
$$M' = (M_{a} + M_{b}) / 2^{\frac{1}{2}}$$

or

Similarly

$$M'' = (M_a - M_b) / 2^{\frac{1}{2}}$$

For the perfect sandwich dimer

$$M'' = 2^{-\frac{1}{2}}(M_a - M_b) = 0$$
$$M' = 2^{-\frac{1}{2}}(M_a + M_b) = 2M_a/2^{\frac{1}{2}}$$

Thus, the transition moments for the dimer are given as superpositions of the transition moments for the individual molecules. The oscillator strength (f) for electric dipole transitions to ψ " is zero, while the transition to ψ ' is equal to

$$f' \propto |M'^2| = |2M_a^2|$$
 or $f' = 2f_{monomer}$

In conclusion we see that for non-polar molecules in the ground state, the interaction energy will be given as a second order correction to the isolated molecule energy. In the excited-ground state case, however, the correction is in first order. For aromatic hydrocarbons the stacked configuration is the least favored in the ground state.

2. Charge-Transfer Interactions

The theory of charge transfer complexes in its present form was developed by Mulliken in 1952.³⁷ Here we are going to discuss some aspects of this theory with emphasis on electronic spectra. For excellent reviews of the subject see the articles of McGlynn,³⁸ Briegleb,³⁹ Murrel⁴⁰ and Mulliken and Pearson.⁴¹

The quantum-mechanical description for the electronic structure of a molecular complex in its ground electronic state is given by ψ_N (N stands for normal state), the wave-function which is the lowest-energy solution of the Schroedinger wave equation for all the electrons in the complex.

Mulliken represented ψ_N for a 1:1 complex in terms of the normal-state wavefunction ϕ_D and ϕ_A of the electron donor (D) and the electron acceptor (A) with corrections because the two partners are close together and interacting. For this purpose, ϕ_D and ϕ_A need not actually be known. In the case that donor and acceptor are evenelectron systems Mulliken writes

$$\psi_{N} = a\phi_{0}(D,A) + b\phi_{1}(D^{+}-A^{-})$$

no bond dative

Here the no-bond wavefunction $\phi_0(D,A)$ is an antisymmetrized product of the wavefunctions ϕ_D and ϕ_A each first corrected for any polarization effects due to possible classical electrostatic forces and to quantum mechanical attractive (dispersion) and repulsive (exchange) forces together with changes in ϕ_D and ϕ_A which result from changes in the internal geometry of D and A upon complexing.

The function ϕ_1 is of Heitler-London type for the hypothetical D^+-A^- pair obtained by removing one electron from an MO in D, putting it into a previously unoccupied MO of A, and possibly forming a weak chemical bond between the odd electrons now situated on the two components of the complex. The ψ_N function is normalized to unity which means that $a^2+b^2+2abS_{01} = 1$ where $S_{01} = \langle \phi_0 | \phi_1 \rangle$. An important property of ϕ_0 and ϕ_1 is of course that they should belong to the same group theoretical symmetry species.

If the ground state of the complex is described by then there is an excited state ψ_V which can be called a charge-transfer (CT) state given by

$$\psi_{\rm V} = -b^{*}\phi_0(D,A) + a^{*}\phi_1(D^{+}-A^{-})$$

The coefficients b^{*} and a^{*} are determined by the requirement that the excited-state wavefunction be orthogonal to the ground state wavefunction. ψ_V is normalized so $a^2 + b^2 - 2a^*b^*s_{01} = 1$ and from the orthogonality requirement $\langle \psi_N | \psi_V \rangle = 0$ follows that $a^* \geq a$, $b^* \geq b$. If $S_{01} = 0$ then $a^* = a$ and $b^* = b$. Since for loose complexes the ground state is mostly no-bond $(a^2 >> b^2)$ and so (because of the orthogonality requirement) the excited state is mostly dative $(a^{*2} >> b^*)$. Excitation of an electron from ψ_N to ψ_V essentially amounts to the transfer of an electron from D to A.

To obtain the exact solution of the Schroedinger equation for the complex is of course not feasible. For this reason we have to use the approximate expression for ψ_N and ψ_V and apply the variation principle. Since both ψ_N and ψ_V are two component linear variation functions the problem is reduced simply to the solution of a two dimensional equation:

 $\begin{vmatrix} H_{00} - E & H_{01} - S_{01}E \\ H_{10} - S_{01}E & H_{11} - E \end{vmatrix} = 0$

where

$$H_{00} = E_0 = \langle \phi_0 | H | \phi_0 \rangle$$
$$H_{11} = E_1 = \langle \phi_1 | H | \phi_1 \rangle$$
$$H_{01} = E_{01} = \langle \phi_0 | H | \phi_1 \rangle$$
$$H_{10} = E_{10} = \langle \phi_1 | H | \phi_0 \rangle$$

Noting that $H_{10} = H_{01}$ the solution of this determinant for E has two roots which are to be identified as E_N and E_V

$$E = \{ \frac{1}{2} (E_0 + E_1) - S_{01} E_{01} \pm [(\frac{1}{2} \Delta)^2 + \beta_0 \beta_1]^{\frac{1}{2}} \} / (1 - S_{01}^2)$$

Here

$$\beta_{0} = E_{01} - E_{0}S_{01} \qquad (\beta_{0} < 0)$$

$$\beta_{1} = E_{01} - E_{1}S_{01} \qquad (\beta_{1} < 0)$$

and $\Delta = E_1 - E_0$ ($\Delta > 0$ usually but sometimes $\Delta < 0$).

The lower energy root is always called E_N (normal state), the upper is E_V , even if $\Delta < 0$. As we said, the complex formation is associated with the appearance of a new absorption band the so called charge-transfer (CT) band. The frequency of the CT band is

$$hv_{CT} = E_V - E_N = 2\{(\Delta/2)^2 + \beta_0\beta_1\}^{\frac{1}{2}}/(1-S_{01}^2)$$

Knowing the energies E_N and E_V we can now obtain the ratio of the coefficients b/a and b^*/a^*

$$\lambda = b/a = -(E_0 - E_N) / (E_{01} - S_{01} E_N) = -(E_{01} - S_{01} E_N) / (E_1 - E_N)$$

and

$$\lambda^* = b^*/a^* = (E_{01} - S_{01}E_V) / (E_0 - E_V) = (E_1 - E_V) / (E_{01} - S_{01}E_V)$$

In this way the wavefunctions can be written

$$\psi_{N} = (\phi_{0} + \lambda \phi_{1}) / (1 + 2\lambda s_{01} + \lambda^{2})$$

$$\psi_{V} = (\phi_{1} - \lambda^{*} \phi_{0}) / (1 - 2\lambda^{*} s_{01} + \lambda^{*2})^{\frac{1}{2}}$$

If $(\Delta/2)^2 >> \beta_0 \beta_1$, and if $S_{01} << 1$ as is expected to be more or less true for weak complexes, the exact expressions above reduce to the following

> $E_N = E_0 + {\beta_0}^2 / \Delta + \text{small correction terms}$ $E_V = E_1 + {\beta_1}^2 / \Delta + \text{small correction terms}$

then

$$hv_{CT} = \Delta + (\beta_0^2 + \beta_1^2) / \Delta + ...$$

the position of the CT band is sometimes used to empirically estimate Δ and $\beta_0^2 + \beta_1^2$. Classically $E_1 - E_0 = I_D - A_A$ - $(\Delta E_D + A^- - \Delta E_D A)$ where I_D is the energy of formation of the D⁺A⁻ structure and $E_D A$ is the energy of formation of the DA structure.

For a series of closely related weak complexes with a single acceptor, the CT relation can be written in the form

$$hv_{CT} = I_{D} - C_{1} + C_{2} / (I_{D} - C_{1})$$

Briegleb showed that experimental v_{CT} values plotted against ID and fitted with curves of the above form can give values of C₁ and C₂. The curve-fitting is moderate (scattered points) and has been applied to various types of complexes, besides Briegleb, by Becker and Chen and Mulliken and Pearson.⁴¹

Alternatively,

$$h_{v_{CT}} = E_{v} - E_{N}$$
$$= I_{D} - A_{A} - (\Delta E_{v} - \Delta E_{N})$$
$$= I_{D} - A_{A} - C$$

where ΔE_V and ΔE_N are the energies of formation of the DA complex in the excited and ground states, respectively, and C is their difference.

The discussion above was describing the situation where D and A are two different chemical species. As D and A become more and more similar we reach the case of a self-complex. In this case the ψ_N between two molecules A which we label as 1 and 2 can be written as

$$\psi_{N} = a\phi_{0}(A_{1}, A_{2}) + b\{\phi_{1}(A_{1}^{+}-A_{2}^{-}) + \phi_{1}(A_{1}^{-}-A_{2}^{+})\}$$

3. Excimer Interaction

In this section we will outline the usual approach for describing the excimer state. We will consider the case of naphthalene excimer which is of immediate interest to us. The first to consider the case of naphthalene excimer theoretically was Th. Forster in 1962. He attributed the excimer binding to be due to exciton coupling. His general model for the excimer formation process in the case of aromatic hydrocarbons was as follows:

(1) The lowest excited singlet state of the monomer should be a ${}^{1}L_{b}$ state, which has a small transition moment to the ground state ${}^{1}A$. The relatively long lifetime of this state allows excimer formation to occur at reasonable monomer concentration.

(2) The ${}^{1}L_{b}$ state should be adjacent to a higher energy ${}^{1}L_{a}$ state, which has a large transition moment to the ground state. The large splitting of the ${}^{1}L_{a}$ state in contrast to the usually small splitting of the ${}^{1}L_{b}$ state results in the lowering of one of the ${}^{1}L_{a}$ exciton components below the lowest ${}^{1}L_{b}$ component, Figure 4. It is the transition from this lowest energy ${}^{1}L_{b}$ component to the ground state which forster attributed the excimer fluorescence. Shortly after it was realized that the exciton coupling cannot account for the excimer binding energy. For the naphthalene excimer in order to account for the binding energy using $\Delta \varepsilon = |M^{2}| / R^{3}$, the physically unacceptable R of 1.8A must be used.

Slifkin ⁴² considered the possible implication of charge resonance states in the excimer emission. By plotting $I-A^{-1}L_b$ vs hv_D for a number of aromatic hydrocarbons he found a linear relationship which made him to suggest that the excimer emission is a charge-transfer emission. The energy of such a charge transfer state can be expressed as $I-A-C\pm R$ (I = ionization potential,

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Figure 3. Exciton Splitting in Molecular Dimers



Figure 4. Exciton Model of Excimer Formation in Aromatic Hydrocarbons

A = electron affinity, C = Coulombic interaction between the resulting charges and R is a term resulting from the interaction of the two possible degenerate charge resonance states).

In the case of naphthalene $I-A = 9.50^{43}$ or 9.74^{44} . Using the point charge approximation, ⁴⁵ C is approximately 3 eV at 3A. So I-A is over 2 eV higher than the energy of excimer fluorescence 3.13 eV⁴⁶ an energy which is too high to be accounted by the resonance energy between the structure A^+A^- and A^-A^+ and the ground state repulsion.

The failure of either the exciton or the chargeresonance model to explain excimer behavior in general led to the introduction of the configuration interaction model by Konijnenberg.⁴⁷ This model which has been adopted by most subsequent authors, considers the singlet excimer state as a "mixed" state produced by configuration interaction of charge-resonance and exciton-resonance state.

Murrel⁴⁸ and McGlynn⁴⁹ used this approach to study the naphthalene excimer.

In the following we will outline how such a treatment goes. The MO picture of naphthalene molecule (D_{2h} symmetry) is as follows if we consider only the transition from the highest occupied MO and the second highest occupied MO.

Symmetry species



Molecule A Molecule B

Let us consider the three lowest energy excited states of the excimer: one charge resonance state and two molecular exciton state, one due to ${}^{1}L_{a}$ monomer state and one due to ${}^{1}L_{b}$ monomer state. The ${}^{1}L_{a}$ state is produced by the excitation of an electron from the highest occupied orbital to the lowest vacant orbital $w_{1} \rightarrow w_{2}$ while the ${}^{1}L_{b}$ state is a resultant of the two zeroth-order degenerate excitation: $w_{1} \rightarrow w_{3}$ and $w_{0} \rightarrow w_{2}$. Molecular exciton states of ${}^{1}L_{a}$ parentage may be expressed by the following two wavefunctions

 $\psi_{\mathbf{A}} = |\mathbf{w}_{1}\overline{\mathbf{w}}_{1}\theta_{1}\overline{\theta}_{2}| - |\mathbf{w}_{1}\overline{\mathbf{w}}_{1}\overline{\theta}_{1}\theta_{2}|$ $\psi_{\mathbf{B}} = |\mathbf{w}_{1}\overline{\mathbf{w}}_{2}\theta_{1}\overline{\theta}_{1}| - |\overline{\mathbf{w}}_{1}\mathbf{w}_{2}\theta_{1}\overline{\theta}_{1}|$

where the bar denotes β spin. Molecular exciton states of ${}^{1}L_{b}$ parentage can be expressed as

$$\psi_{\mathbf{C}} = |\mathbf{w}_{1}\overline{\mathbf{w}}_{1}\theta_{0}\overline{\theta}_{2}| - |\mathbf{w}_{1}\overline{\mathbf{w}}_{1}\overline{\theta}_{0}\theta_{2}| + |\mathbf{w}_{1}\overline{\mathbf{w}}_{1}\theta_{1}\overline{\theta}_{3}| - |\mathbf{w}_{1}\overline{\mathbf{w}}_{1}\overline{\theta}_{1}\theta_{3}|$$
$$\psi_{\mathbf{D}} = |\theta_{1}\overline{\theta}_{1}\mathbf{w}_{0}\overline{\mathbf{w}}_{2}| - |\theta_{1}\overline{\theta}_{1}\overline{\mathbf{w}}_{0}\mathbf{w}_{2}| + |\theta_{1}\overline{\theta}_{1}\mathbf{w}_{3}\overline{\mathbf{w}}_{3}| - |\theta_{1}\overline{\theta}_{1}\overline{\mathbf{w}}_{1}\mathbf{w}_{3}|$$

Finally for the charge resonance states

$$\psi_{\mathbf{E}} = |\mathbf{w}_{1}\overline{\theta}_{2}\theta_{1}\overline{\theta}_{1}| - |\overline{w}_{1}\theta_{2}\theta_{1}\overline{\theta}_{1}|$$
$$\psi_{\mathbf{F}} = |\mathbf{w}_{1}\overline{w}_{1}\mathbf{w}_{2}\overline{\theta}_{1}| - |\mathbf{w}_{1}\overline{w}_{1}\overline{w}_{2}\theta_{1}|$$

Linear combinations of the above wavefunctions transform according to irreducible representations of the D_{2h} group

$${}^{1}L_{a} \qquad {}^{B}_{3g}: \quad \psi_{A} - \psi_{B}$$

$${}^{B}_{2u}: \quad \psi_{A} - \psi_{B}$$

$${}^{B}_{2u}: \quad \psi_{C} - \psi_{D}$$

$${}^{B}_{3u}: \quad \psi_{C} - \psi_{D}$$

$${}^{B}_{3u}: \quad \psi_{C} - \psi_{D}$$

$${}^{B}_{3g}: \quad \psi_{E} - \psi_{F}$$

$${}^{B}_{2u}: \quad \psi_{E} - \psi_{F}$$

From these results one sees that for a D_{2h} excimer the ${}^{l}L_{a}$ exciton states transform in the same way as the chargeresonance state while ${}^{l}L_{b}$ exciton states transform differently from both ${}^{l}L_{a}$ exciton and charge-resonance states.

To determine the energy of the excimer state the validity of the separability approximation is usually assumed. In this approximation the Hamiltonian of the system can be written as

$$H = H_{core} + \sum_{v < u} 1/r_{vu}$$

where $1/r_{vu}$ is the electrostatic repulsion between

electrons v and u and $H_{core} = \sum_{v}^{H} H_{core}$ (v) where H_{core} (v) represents the effect of the core on electron v.

For the D_{2h} excimer, from our previous considerations, there is nonvanishing configuration interaction between $|B_{2u}(exc) > and |B_{2u}(CR) > and between |B_{3g}(exc) > and$ $|B_{3g}(CR) > states. So the problem reduces to the solution$ of secular equations of the form

where for example

$$H_{12} = \langle (exc) | H | (CR) \rangle$$

 $S_{12} = \langle (exc) | (CR) \rangle$

McGlynn and Murrell used different methods to evaluate the matrix elements involved and especially matrix elements of the type $\langle (exc) | H | (exc) \rangle$ but both concluded that the lowest excimer state is of B_{3g}^- symmetry and that the other excimer states in order of increasing energy are B_{2u}^- , B_{2u}^+ and B_{3g}^+ . Both calculations give an interplanar distance of about 3Å. These semiempirical techniques although useful in providing us with "physical" concepts do not give results of quantitative significance.

A "supermolecule" approach where the whole excimer is treated as one entity, molecule, with the technique of molecular orbitals would be desirable. Moreover the ab initio approach is needed. At this moment this approach appears technically unrealistic. Buenker and Peyerimhoff⁵⁰ performed ab initio calculations on naphthalene. Even with an inflexible basis C(10s, 5p/3s, 1p) and H(5s/1s)they had to compute 0.89 billion electron repulsion or two-electron integrals. Probably an approach like the "molecule in molecules" of von Niessen;⁵¹ where the wavefunction of a molecule is constructed from the wavefunctions of fragments structurally related to the molecule may be useful for constructing excimer states.

Up to now only semiempirical supermolecule calculations have been performed. In this way Azumi⁵² used a simple Huckel treatment for the naphthalene excimer while Lim^{53} used Huckel orbitals and limited configuration interaction among several states. The calculated interplanar distance was again 3\AA .

CHAPTER II

PROTON TRANSFER IN THE EXCITED STATE OF \alpha-CARBOLINE HYDROGEN-BONDED DIMER AND ITS ACETIC ACID COMPLEXES

A. Introduction

It has been shown by Forster,⁵⁴ that many aromatic compounds display an acidity in the excited state very different from that in the ground state because of electron density⁵⁵ redistribution in the molecule after excitation. The change in electron density may enhance or decrease proton dissociation. In some cases, an acid-base equilibrium in the excited state completely independent of that in the ground state is achieved.

The study of the emission and absorption spectra is a gauge by which the change in acidity upon excitation can be detected. Such a change is detectable only if the rate constant for proton transfer in the excited state is comparable to or greater than the rate of decay of fluorescence. In this case, the absorption spectra exhibit a pH dependent different from that of the fluorescence spectra so that the ground state and excited state may be characterized by different pk_a value. From the spectral shift in absorption and emission spectra,^{56,57} Weller estimated the value of $pk_a^* - pk_a$ using the following

relation

$$pk_{a}^{*} - pk = \frac{0.625}{T} \Delta \overline{v}_{a} (cm^{-1})$$

Compounds that change their pk value as a result of excitation can be divided into two groups: one with decreasing pk_a values after excitation, such as ArOH, ArNHR, ArNHRR', ArSH, ^{58,59,60} and the other group with increasing pk_a values such as ArCOOH, Ar-d=0, $Ar-d=N^{-R}$, Ar N: ^{61,62}. Sometimes the pk_a value decreases by six or seven units and therefore, the molecules are able to undergo a proton transfer reaction which doesn't occur in the ground state.

The study of the excited state behavior of β -naphthol and 3-hydroxyl pyrene⁶³ present good examples for demonstrating excited state proton transfer. The absorption spectra are not solvent dependent, contrary to the behavior of emission spectra. The emission of β -naphthol in the triethylamine is shifted to the red by 700 cm⁻¹ with respect to that in methylcyclohexane. A similar shift with 500 cm⁻¹ has been observed in 3-hydroxypyrene triethylamine system. The large shift in the emission can be explained in terms of proton dissociation in the excited state as the associated spieces of the complex is more basic. In other words, the decrease of pk_a value of the molecule is not only dependent on the excitation of the molecule itself but also dependent on the basicity of the associated species of the complex which is formed after the excitation or before the excitation.

Some literature data about pk_a^* and pk_a values are listed in the following table for comparison

	pk	pk-pk
phenol	10	4.3
a-naphthol	9.23	7.23
β-naphthol	9.46	6.65
3-hydroxypyrene	8.7	5.0
4-ammonium pyrene (in ethanol)	3.7	5.5
3-ammonium pyrene 5,8,10 trisulphonate	2.6	9.7
2-naphthol-5-sulphonate	9.18	8.65
2-naphthol-6-sulphonate	9.00	7.50
acridinium cation	5.45	4.85
benzoic acid cation	-7.2	-6.0
acetophenone cation	-6.0	-9.0

The ratio of the amount of protonated species and deprotonated species in the excited state can be estimated from the intensity of their respective emission bands. It is dependent upon solvent polarity and temperature.

A more detailed picture of proton transfer has been given by Weller. 64 The proton transfer in solution from an acid AH^{*} to a base B occurs in the following steps:

$$AH^{+}B \xrightarrow{\text{diffusion}} AH^{+}...B \xrightarrow{\text{PT}} A^{-*}...HB \xrightarrow{\text{diffusion}} A^{-*}+HB^{+}$$
(1)
(2)
(3)

The ratio of the first and the third step depend on the diffusion coefficients of the species, and on the dielectric constant of the medium when both species are ions. The second step in the key step for the actual proton transfer reaction. It is dependent upon the polarity and orientation of acceptor.

From rate study of protolysis of ammonium derivative of pyrene at various temperatures, it was found that the reaction velocity and its temperature coefficient depend on the nature of solvent, but not on the strength of the acid which varied from $10^2 \ 10^6$ mole/ ℓ . This could be explained only by the assumption that the rearrangement of the surrounding solvent molecules prior to the proton transfer is the rate determining step.

For the role of solvent on excited state proton transfer one may deal with two cases. The first one is the intermolecular proton transfer occurring in the solution of β -naphthol and triethylamine. The increase of solvent polarity is favorable to the deprotonated side of the equilibrium. This is due to the ion pair formation after the proton transfer.⁶⁵ The second case, is intramolecular proton transfer occurring in the salicylic ester and its derivatives. As the solvent polarity increases, the equilibrium will shift to the protonated side. This is due to the decrease of dipole moment by introducing the charge transfer in the excited state.

The change in temperature may shift the excited state equilibrium depending on the enthalpy change, e.g., ΔH in the excited state. From experience, it mainly depends on the substituent on the molecule.⁶⁶ For proton transfer in salicylic ester, it is exothermic with ΔH is -0.7 Kcal/mole. On the other hand, proton transfer process in 5-ethoxyl-salicylic ester is endothermic with ΔH is 0.9 Kcal/mole. Therefore, the decrease of temperature will be favorable to the protonated side.

Intramolecular proton transfer is usually more efficient than the intermolecular proton transfer because of the closeness of the two functional groups, one with increasing acidity, the other with increasing basicity during the excitation. In the case of salicylic acid, the proton in the OH group becomes dissociated more easily and the oxygen in the carbonyl group becomes more basic to accept the proton. This mutually opposite effect in the excited state enhances the rate of proton transfer. A similar situation occurs in the case of 7-azaindole hydrogen bonded dimer which has been studied in EL-Bayoumi's Lab.⁶⁷ The acidity of pyrrolic proton increases as the basicity of the pyridinal lone pair electron increases. As a result efficient double proton transfer occurs in the excited state, which can be easily identified by the emission of resulting tautomer.

In order to understand the phenomenon of excited state double proton transfer, we searched for systems

which have favorable fluorescence properties particularly long fluorescence lifetimes in order to examine the dynamics of proton transfer. Thus, I have studied α -carboline (1-aza-carbazole) hydrogen-bonded dimer and its acetic acid complex. I was interested in the static as well as dynamic properties of proton transfer itself. My aim is to obtain the value of the rate constant and estimate the energy barrier for proton transfer.

Since DNA base pair has two kinds of hydrogen bonds, one being NH....N, the other being NH....0, the α -carboline hydrogen-bonded dimer and its acetic acid complex are useful model systems.

B. Excited State Proton Transfer in α -Carboline Hydrogen Bonded Dimer

The emission of α -carboline in 3 methylpentane with concentration around 10^{-4} or 10^{-5} M exhibits only one band with a maximum intensity at 367 nm. A concentrated $(10^{-3}M)$, however, exhibits two emission bands. The first band which we may call F_1 band is very similar to the one in dilute solution. The new band which we may call F_2 band is a broad band with a maximum intensity around 510 nm (See Figure 5).

The intensity of the F_2 band is not only concentration dependent, but it also depends on temperature and the excitation wavelength. The first question that we concern was the origin of F_2 band. To be able to answer this question, we have examined the absorption and emission



Room temperature fluorescence spectra of α -carboline in 3 methylpentane at two different concentrations 2.5 x 10⁻⁴M ----- , 2.5 x 10⁻³M ---- --- --- . Fig. 5.

properties of α -carboline under various conditions.

1. Solvent Effect on the Room Temperature Absorption Spectra of *a*-Carboline

The room temperature absorption spectrum of α -carboline solution in 3-methylpentane (2.5 x 10^{-3} M) is shown in Figure 6. The absorption band covering the range from 300 nm to 350 nm corresponds to the transition A to L_{b} state, and its transition depolemoment is along the short axis which lies on the nitrogen atom of the pyrrole position of the molecule. The other absorption band with a maximum at 296 nm corresponds to the transition to the L_s state, its transition dipolemoment lies along the long axis such assignment will be obtained from emission polarization data. The structure of α -carboline is similar to that of carbazole except that the CH in the one position has been replaced by an aza nitrogen. In comparing the absorption spectrum of α -carboline with that of carbazole we find that they are very similar. It indicates that the aza nitrogen has a little effect on the $\pi + \pi^*$ electronic transitions and that possible $n+\pi^{*}$ transitions in the spectral region covered are probably submerged under the more intense $\pi + \pi^*$ transition.

The carbazole absorption spectra has been studied in various solvent primarily due to hydrogen bond formation occurring between the pyrrolic hydrogen atom and the lone pair electron of the other or alcohol solvent molecules. Both the L_a and the L_b bands are shifted to





red. The red shift of L_b band is larger than that of the L band, the values are listed in Table 1. The average shift of the L_a band is 230 cm^{-1} and average shift of the L_{h} band is 460 cm⁻¹. This indicates that the hydrogen bond strength has the follow order $L_b > L_a$. The α -carboline molecule has an azanitrogen in addition to the pyrrolic nitrogen. Thus, it has the capacity to form an additional hydrogen bond with proton of alcohol or acetic acid. This explains the observation that the absorption bands of a-carboline are shifted more to the red in alcohol solvent compared with carbazole. The average red shift of L band is 770 cm⁻¹ and the average shift of the L_b band is 1350 cm^{-1} , which is almost three times larger than that of carbazole and the spectra are shown in Figure 11, 7. Furthermore, the 250 nm band is red shifted also. One concludes that the acidity of the pyrrolic proton and the basicity of the aza nitrogen of α -carboline are both enhanced particularly in the L_b state, the lowest excited singlet state.

2. Solvent Effect on the Room Temperature Emission Spectra of α-Carboline

The room temperature emission spectra of α -carboline have been measured in different media and are shown in Figure 8. The larger shift of the emission maximum compared with corresponding shifts of the absorption maximum reflects the relaxation that occurs in the excited

or N-ethylcarbazole, carbazole,	
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Table	

	Ц ^Ч И	ethylcarba	zole		Cabazole		8	Carbolin	
	MCH	Ethanol	۵۷ (حس ¹)	MCH	Ethanol	۵۷ (حس ¹)	Monomer	Dimer	۵۷ (cm ⁻¹)
'A+'Lb	29070	28985	85	30120	29674	446	29674	28328	1346
	30488	30303	153	31348	30864	684	30675	29412	1263
	31446	31250	196	32573	32051	522	31847	30303	1564
'A+'La	34072	34072	0	34329	34072	257	33445	32787	658
	34782	34722	61	35088	34783	305	34129	33557	572
	35398	35336	62	35589	35336	251	34722	33898	824

* MCH = methylcyclohexane







Fig. 8. Room temperature fluorescence spectra of α -carboline (10⁻⁵M) in different media: ----- cyclohexane, ----- ether, ------ ethanol

state before fluorescence, see Table 2. The loss of fine structure in ethanol is due to the various possible interactions between the solute and polar solvent molecules.

3. pH Effect on a-Carboline Fluorescence

The large redistribution of electron density as a result of excitation, is reflected in the large value of the $\Delta\mu$, e.g., the dipolemoment change. Consequently, the acidity and basicity of the molecule in its first excited state is different from that of the ground state.

We have measured the absorption and emission spectra of α -carboline in water at different pH values. In the pH range from 7 to 13, both the absorption spectra and emission spectra show no change. Above the pH value of 13, the absorption spectra remains the same, however, the emission spectrum exhibits the 400 nm band as well as a shoulder in the 500 nm region (see Figure 9). The new emission band can be clearly identified as the emission of anion of α -carboline which exists in pH>14 solution.

From the above discussion, we can conclude that the acidity increases upon excitation to the L_b state. In other words, the proton will dissociate more easily in the lowest excited singlet state than the ground state. Other evidence that supports our idea is the dramatic decrease of fluorescence quantum yield around pH 13.5 (see Figure 10) which is due to the proton dissociation of the pyrrolic nitrogen and production of the weakly

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Absorption a
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Table

	Emission Maxima (nm)	∆ <u>√</u> (cm ⁻ ¹)	Absorption Maxima (nm)	∆√(cm ⁻¹)	Stokes Shift (cm ⁻¹)
Cyclohexane	360	o	326	o	2890
Ether	369	677	328	490	3390
Ethanol	378	1322	330	916	3850
$\Delta \overline{V}(cm^{-1})$ are st	lifts using cycl	ohexane as a	reference.		
Stokes shift aı given solvent.	e the differenc	e between flu	orescence and at	sorption maxi	ma in a





Relative Intensity

emitting anion. The actual magnitude of the pk_a value change due to excitation has been estimated using the Forster cycle to be around 10 units. The Δpk_a of indole, is 4.6.

4. Equilibrium Study of α-Carboline Hydrogen Bonding Dimerization

The hydrogen bonding dimer formation of α -carboline has been studied by comparing the U.V. absorption spectra at different concentration in 3-methylpentane at room temperature. The L_b band at two concentrations are shown in Figure 11. A shoulder appears at 353 nm in the more concentrated solution, this shoulder becomes more pronounced at lower temperatures where more dimer are formed.

One may obtain the association constant from the following formula:

$$\frac{C}{A} = \frac{2}{\varepsilon} + \left(\frac{1}{\varepsilon K}\right)^{\frac{1}{2}} \left(\frac{1}{A}\right)^{\frac{1}{2}}$$

where

C is the total concentration of α -carboline

 ε is the absorption coefficient of dimer

A is the absorbance in 353 nm

K is the equilibrium constant of dimerization The dimer association constant in 3 m.p. is 6.8 x 10^{-2} M⁻¹ at room temperature (21°C), 8.1 x 10^{-3} M⁻¹ at 0°C, $\sim 10^{8}$ at 77°K the $\Delta H = -18.25$ Kcal/mole. The large negative value of enthalpy means the system is favorable to dimerize at



Fig. 11. Room temperature ultraviolet absorption of α -carboline in 3 methylpentane at different concentration: -2×10^{-5} M in 10 cm cell, $----- 2 \times 10^{-4}$ M in 1 cm cell

low temperature. One conclusion derived from the U.V. study is very interesting and probably important, too. That is the absorption coefficient for the dimer is almost the same as the monomer absorption coefficient 4×10^3 cm⁻¹ M⁻¹. In other words, the hydrogen bond shifts the absorption band, but does not change the transition dipolemoment of the band.

I.R. spectra has been used also to study the hydrogen bonding dimerization. In carbon tetrachloride with a concentration of 10^{-3} M, the free N-H stretching band with a frequency at 3480 cm⁻¹ is pronounced. As the concentration is increased, the broad band at lower frequencies increase in relative intensity (see Figure 12). This broad band has fine structure of 80 cm⁻¹ spacing which can be explained in terms of coupling motion between the stretching mode of NH....N and the bending mode of the whole hydrogen bond dimer. One may obtain the association constant from the following formula:

$$\frac{C}{A} = \left(\frac{2K}{k^2}\right)A + \frac{1}{k}$$

C is total concentration

A is the absorbance at 3480 cm^{-1}

K is the equilibrium constant

k is the path length in cm times the molar extinction coefficient of the free N-H stretching

By plotting C/A with respect to A, one gets a value of K of ~100% /mole at 31°c.



5. Excitation Spectra of the F₁ and F₂ Bands

The study of excitation spectra can reveal the source of a given emission band. Excitation spectra of α -carboline F_1 and F_2 fluorescence band are shown in Figure 13. By fixing the emission wavelength at the maximum of the F_1 band or that of the F_2 band the excitation wavelength is scanned. A comparison of both excitation spectra that covers the range from 290 nm to 375 nm reveals that the F_1 excitation spectrum has a maximum at approximately 325 nm which corresponds to the maximum absorption of the L_b band. In the F_2 excitation spectrum that maximum shifted to longer wavelength (335 nm) approximately corresponding to the shift of the absorption spectra when the concentration is increased (see Figure 6). Therefore, the F_2 band originates from the hydrogen bonded dimer of α -carboline while the F_1 band arise from the α -carboline monomer. Furthermore, the peak at 305 nm in the excitation spectrum for concentrated solution just correspond to the absorption maximum of L_a band of the dimer absorption (see Figure 7).

6. Evidence of Double-Proton Transfer in α -Carboline Dimer

The assignment of the F_2 band as being due to a tautomer (see Figure 14) formed as a result of double proton transfer in the excited state can be further confirmed by synthesizing that tautomer or a derivative of it and study its emission spectra. Therefore, we have synthesized the N₁-methyl tautomer of α -carboline which is









Fig. 14. Double proton transfer in α -carboline dimer and α -carboline acetic acid complex
stable and has the same conjugated system as the proposed tautomer. Its emission spectra in various solvents has been examined and is shown in Figure 15. Emission spectra in ethanol and in water are almost the same as the F_2 band obtained by the excitation of the carboline dimer. The luminescence study of a similar system, 7-azaindole dimer and its methyl tautomer, has been done in our lab at 77°k. The fine structure in emission band of the synthesized tautomer and the F_2 band is similar.

From the above discussion we have concluded that the F_2 band arises from a tautomer formed from the excited state of α -carboline hydrogen bonded dimer as a result of an excited state double proton transfer.

7. Dynamics of Double Proton Transfer

Since the proton transfer in the excited state may be too fast to be followed with our nanosecond timeresolved set up. We have deuterated α -carboline at the pyrrolic nitrogen. To further slow down the proton transfer process, our measurements will be performed at 77°k. The flash deuteron lamp is the light source we have used. The signal from 1p28 photomultiplier starts the sweep in the time amplitude converter. The emission from the sample is detected by a single photon count tube DUVP56. The high voltage output will stop the sweep in the time amplitude converter. The signal is, the larger amplitude it will become. By using the



--- ether, ----- 3-methylpentane temperature in different media: ethanol, ----- ether, -----

...

multichannel analyzer, the signals will be arranged into the memory according to the pulse height of the output. As the time passes, the data will be accumulated in the channels. The lamp curve, the F_1 decay curve, and the F_2 decay curve were shown in Figure 16. The F_1 and F_2 decay curve are not truly decay curves, since they contain the excitation pulse. After deconvolution, the true decay curve for F_2 has been obtained. the double exponential curve is shown in Figure 17. One is with a lifetime of 3.9 nsec (τ_1) and the other with a lifetime of 12.1 nsec (τ_2) .

Suppose the reciprocal of τ_1 is λ_1 and the reciprocal of τ_2 is λ_2 . In order to obtain the rate constant for proton transfer k_{TD} , we prepare the following scheme.



D -- hydrogen bonded dimer of α -carboline

T -- tautomer after proton transfer

K_{FD} -- fluorescence rate const. for dimer

K_{ID} -- radiationless transition rate constant of dimer

 $K_{\rm FT}$ -- fluorescence rate constant for tautomer

K_{IT} -- radiationless transition rate constant of tautomer



Fig. 16. Decay curve of α -carboline dimer, upper-lamp curve, middle-decay curve of F₁ band, bottom--decay curve of F₂ band



Fig. 17. Double exponential decay curve of the F₂ band (10 channel per division, 0.0383 nsec per channel)

$$K_{D} = K_{FD} + K_{TD}$$

$$K_{T} = K_{FT} + I_{IT}$$

$$\frac{dD^{*}}{dt} = -k_{TD}(D^{*}) - k_{FD}(D^{*}) - k_{ID}(D^{*}) + k_{DT}(T^{*})$$

$$= -[k_{TD} + k_{FD} + k_{ID}] (D^{*}) + k_{DT} (T^{*})$$

$$= - x(D^{*}) + k_{DT}(T^{*})$$

$$\frac{dT^{*}}{dt} = -k_{DT}(T^{*}) - k_{FT} (T^{*}) - k_{IT} (T^{*}) + k_{TD} (D^{*})$$

$$= -[k_{DT} + k_{FT} + k_{IT}] (T^{*}) + k_{TD} (D^{*})$$

$$= - y(T^{*}) + k_{TD} (D^{*})$$

Assume the decay time λ_1 , λ_2

$$D^{*} = Ae^{-\lambda_{1}t} + Be^{-\lambda_{2}t}$$
$$T^{*} = Ce^{-\lambda_{1}t} + De^{-\lambda_{2}t}$$

at beginning t = o, $D^* = D_0^*$, $T^* = o$

$$D_{0}^{*} = A + B, C + D = 0$$

$$\frac{dD}{dt}^{*} = -A\lambda_{1}e^{-\lambda_{1}t} - B\lambda_{2}e^{-\lambda_{2}t}$$

$$\frac{dT}{dt}^{*} = -c_{1}e^{-\lambda_{1}t} - D_{2}e^{-\lambda_{2}t}$$

Same way for

.

$$A = \frac{\frac{D_0^* (A_2 - x)}{\lambda_2 - \lambda_1}}{\lambda_2 - \lambda_1}$$

$$B = \frac{D_0^* (x - \lambda_1)}{\lambda_2 - \lambda_1}$$

$$C = \frac{D_0^* (k_{TD})}{\lambda_2 - \lambda_1}$$

$$\lambda_1 = y - k_{TD} (A) / C$$

$$\lambda_2 = y - k_{TD} (B) / D$$

$$\lambda_1 + \lambda_2 = 2y - k_{TD} \left(\frac{\lambda_2 - x}{k_{TD}} - \frac{x - \lambda_1}{k_{TD}}\right)$$

$$= 2y - (\lambda_1 + \lambda_2 + 2x)$$

$$\lambda_1 + \lambda_2 = X + Y = k_D + k_T + k_{DT} + k_{TD}$$

$$k_{TD} A = (-\lambda_{1} + y)c$$

$$(X - \lambda_{2})B = k_{DT}D$$

$$(-\lambda_{1} + y) (X - \lambda_{1}) = k_{TD} k_{DT}$$

$$(X_{1})^{2} + (X + y) + xy = k_{TD}, k_{DT}$$

$$(\lambda_{1})^{2} + (\lambda_{1} + \lambda_{2}) + xy = k_{TD} k_{DT}$$

$$(-\lambda_{1})e^{-\lambda_{1}t} + (-B\lambda_{2})c^{-\lambda_{2}t} = -(x) (Ae^{-\lambda_{2}t} + Be^{-\lambda_{1}t}) + k_{DT}(Ce^{-\lambda_{1}t} + De^{-\lambda_{2}t})$$

so that

$$-A\lambda_1 = -xA + k_{DT}C$$

 $-B\lambda_2 = x XB + k_{DT}D$

same way

$$-C\lambda_{1} = -yc + k_{TD} A$$

$$-D\lambda_{2} = -yD + k_{TD} B$$

$$(-\lambda_{1} + y)C = k_{TD}A$$

$$(-\lambda_{1} + y)D = k_{TD} B$$

$$(-\lambda_{1} + y)C + (-\lambda_{2} + y)D = k_{TD}A + k_{TD}B = k_{TD}D_{0}^{*}$$

$$(-\lambda_{1} + y)(-D) + (-\lambda_{2} + y)D = k_{DT}D_{0}^{*}$$

$$D(-\lambda_{2} + y + \lambda_{1} - y) = k_{TD} D_{0}^{*}$$

$$D = \frac{k_{TD}D_{0}^{*}}{\lambda_{1}-\lambda_{2}}$$

$$\lambda_{1}\lambda_{2} = xy - k_{TD} k_{DT}$$

$$\lambda_{1}\lambda_{2} = k_{TD} k_{T} + k_{D} k_{DT} + k_{D} k_{T}$$

The k_{TD} can be estimated from measuring the lifetime of N_1 - methyl α -carboline. Its value is 7.00 x 10⁷ sec⁻¹, k_D can be estimated from the lifetime of α -carboline and its quantum yield, it is about 1.8 x 10⁸ sec⁻¹. From these lifetime data, we get (see Figure 18)



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$$\lambda_{1} + \lambda_{2} = k_{D} + k_{T} + k_{DT} + k_{TD}$$
$$\lambda_{1} \quad \lambda_{2} = k_{TD} \quad k_{T} + k_{D} k_{DT} + k_{D} k_{T}$$

$$k_{TD} = 6.1 \times 10^7 \text{ sec}^{-1}$$

 $k_{DT} = 2.1 \times 10^7 \text{ sec}^{-1}$

$$\Delta H^{\ddagger} = 2.95 \text{ Kcal /mole}$$

Fig. 18. Kinetic scheme for proton transfer

$$k_{TD} = 6.1 \times 10^{-7} \text{ sec}^{-1}$$

 $K_{DT} = 2.1 \times 10^{7} \text{ sec}^{-1}$

The rate of proton transfer in α -carboline is slower than that in the 7-azaindole system.

8. Energy Barrier for Double Proton Transfer

The ratio of the intensity of the F_2 band to that of F_1 band, F_2/F_1 is dependent upon temperature. The lower the temperature is, the less the F_2/F_1 ratio becomes. Consequently, the energy barrier for proton transfer in the excited state can be estimated by studying the temperature effect on the F_2/F_1 ratio, several spectra at different temperature and shown in Figure 19.

Suppose:

$$F_{1} = G_{1}k_{D} \left(\frac{k_{FD}}{k_{FD} + k_{ID} + k_{TD} + k_{DT}} \right) = G_{1}k_{D}k_{FD}I_{D}$$

$$F_{2} = G_{2}k_{D} \left(\frac{k_{DT}}{k_{FD} + k_{ID} + k_{TD} + k_{DT}} \right) + \left(\frac{k_{FT}}{k_{FT} + k_{IT}} \right)$$

$$= G_{2} k_{D} \tau_{D} k_{TD}$$

 $F_2/F_1 = (G_2/G_1) (\phi/k_{FD}) k_{PT}$

 k_D is the rate constant for excitation of dimer τ_D is the fluorescence lifetime of the dimer

G is the correction factor for the whole detector system, including the geometrical arrangement of cell and phototube response





Barrier for proton tunneling

 k_{FD} is the rate constant of dimer fluorescence. Since both ϕ and k_{FD} are temperature independent, the F_1/F_2 will be proportional to the k_{PT} . According to the absolute rate theory

$$k_{PT} = A \exp (-Ea/RT)$$

Ea is the activation barrier for double proton transfer. Combining the two equations above, one will obtain the

$$\log F_2/F_1 = const - \frac{Ea}{2.303 \text{ RT}}$$

In the temperature study, we start from room temperature and cool the system gradually. The initial increase of the ratio of F_2 to F_1 is due to the increase in the association constant. The F_2/F_1 ratio reaches a maximum value around 0°c to -10°c, then it decreases since the thermal energy gradually becomes lower than the energy barrier. From the plot of the log of the ratio of F_2 to F_1 (see Figure 20), with respect to 1/T, a value of 2.95 Kcal/mole, the activation energy has been established.

Using this activation energy value and k_{TD} previously obtained one may obtain a value of 10^{13} for the frequency factor A in equation of absolute rate; which is similar to the expected theoretical value $10^{12} \sim 10^{13}$.



Fig. 20. The plot of log F_1/F_2 vs I/T

C. Excited State Proton Transfer in α -Carboline Acetic Acid Complex

 α -carboline forms a complex with acetic acid. The room temperature absorption spectra of α -carboline dilute solution in hexane 2 x 10⁻⁵M in the presence of various amounts of acetic acid are shown in Figure 21. By studying the optical density of the band 353 nm, which attributes to the complex and by using the following formula, one may obtain the association constant of the complex.

$$\frac{C_{A}}{A} = \frac{C_{A}}{C_{2}\ell\varepsilon} + \frac{1}{\varepsilon\ell kC_{2}}$$

 C_A is the concentration of acetic acid C_2 is the concentration of α -carboline K is the association constant

 ε is the absorption coefficient

A plot of CA/A vs l/ELC gives a straight line as shown in Figure 22. From such a plot a value of $10^5 \sim 10^6$ L/M has been estimated for association constant of the complex. It is clear that the association constant of the α -carboline acetic acid complex is much larger than that of α -carboline dimer.

The room temperature emission spectra of 5 x 10^{-4} M $_{\alpha}$ carboline in the presence of excess acetic acid exhibits only the F₂ band as shown in Figure 23. Similarly, at 77°k only F₂ emission is observed. It means that the proton transfer is much faster than the fluorescence rate of α -carboline (4.2 nsec.). The estimated value for k is



Fig. 21. Room temperature absorption spectra of α -carboline (2 x 10⁻⁵M) in hexane, in presence of variable amount of acetic acid, 0, 1.66 x 10⁻⁶, 3.32 x 10⁻⁶, 4.98 x 10⁻⁶, 6.64 x 10⁻⁶, 8.30 x 10⁻⁶, 9.96 x 10⁻⁶, 1.16 x 10⁻⁵M







1.4 x 10^9 sec^{-1} , so that the activation energy in the excited state must be less than 0.16 Kcal/mole and consequently, the thermal energy at 77°k is enough to overcome the barrier (see Figure 23).

D. Conclusion

 α -carboline hydrogen-bonded dimer undergoes an excited state double proton transfer. This manifests itself in a new fluorescence band at 510 nm. The enhanced acidity of the pyrrolic proton and basicity of the azanitrogen in the lowest excited state of α -carboline (${}^{1}L_{b}$ state) makes the proton transfer process favorable. The rate of the proton transfer has been measured to be 6.1 x 10⁷ sec⁻¹ and the energy barrier is estimated to be 2.95 Kcal/mole. The α -carboline-acetic acid complex undergo also an excited state proton transfer that is much more efficient than in the α -carboline dimer.

CHAPTER III

CHARGE TRANSFER, EXCIPLEX, EXCIMER INTERACTION IN DIPHENYL PROPANE DERIVATIVES

A. Introduction

Besides concentration quenching, it was observed that many organic compounds exhibit a charge in fluorescence spectrum, i.e., a new component 5000 cm⁻¹ to 6000 cm⁻¹ red shifted becomes evident with increasing concentration. Since no corresponding change is observed in the absorption spectrum, the new emission species is a dimer which exists in the excited state^{68,69} and dissociates immediately after emitting a proton. A broad diffused fluorescence shifted to the red is characteristic of "excimer emission."

While a dilute solution of pyrene exhibits a structured fluorescence spectrum that extends from ultraviolet to violet region. A concentrated solution exhibits an additional structureless component in the blue region. The blue fluorescence component is attributed to pyrene excimers.^{70,71}

The following kinetic scheme represents a system that undergoes excimer formation.



k_a = association rate constant
k_d = dissociation rate constant
k_s', k_s = radiative rate constants of the monomer and
the excimer respectively
k_s', k = radiationless rate constants of the monomer

 k_{ℓ} ', k_{ℓ} = radiationless rate constants of the monomer and the excimer respectively

$$C_{k} = \frac{k_{s} + k}{k_{a}} = half value concentration$$

The association reaction rate has to be very fast, since the lifetime of the monomer in excited state is in the nanosecond range. The process of excimer formation is diffusion controlled, with both K_a and C_h depending on the viscosity of the solvent. The kinetic and thermodynamic parameters of excimer formation has been derived from a study of temperature effects. The enthalpy ΔH of dissociation of the excimer is between 10 and 11 Kcal/mole in various solvents.⁷² From the fluorescence lifetime study, the entropy of dissociation of the excimer is estimated to be 20 cal/deg mole. These values indicate a strong bonding and a rigid configuration for the excimer of pyrene.

After the discovery of excimer formation for pyrene, the same phenomenon was found to exist in other compounds such as: benzene,⁷³ naphthalene,^{74,75} benzanthracine⁷⁶ anthranthrene, and a large number of derivatives,⁷⁷ including substituted anthracenes.^{78,79} However, in comparison to pyrene, the dissociation enthalpies for these compounds are low, e.g., 5-6 Kcal/mole for both benzene and for naphthalene.^{80,81} If the compound has an alkyl substituent, it will reduce these values even further due to steric hindrance. The dissociation entropies, on the other hand, are similar in magnitude to those of the pyrene excimer (\cong 20 cal/deg mole).

If two or more aromatic residues are flexibly linked to each other by an aliphatic carbon chain, it should be able to form an intramolecular excimer; their fluorescence spectra should contain an excimer component that is independent of concentration. According to Hirayama,⁸² who studied di and triphenylalkances, the composite system with exactly three carbon chains forms excimers. The intensity ratio of the excimer and monomer emission depends on the solvent, not on concentration. Their absorption spectra are normal and resemble those of alkyl benzene, without any ground state interaction. Solutions of polystyrene and of polyvinylnaphthalene,⁸³ in which the aryl group are again linked by aliphatic chains of three carbon atoms, give

fluorescence spectra containing both nomomer and excimer components at room temperature. Nucleic acids and synthetic di and polynucleotides also exhibit excimer fluorescence.⁸⁴ In paracyclophanes, two phenyl groups are linked by methylene chains in both paraposition.^{85,86} The fluorescence spectrum of (4.4) paracyclophane shows only the excimer component, while those of (4.5) - and (6.6) paracyclophane contain practically no excimer component. All these compounds have normal absorption spectra. For a composite system, such as crystal, where the fluorescence is monomer or excimer depends upon the orientation of molecules within the crystal, if the adjacent molecules are oriented almost perpendicular to one another, the fluorescence is like that of the monomer. In the case of molecular crystals where the molecules are either arranged in pairs or stacked in columns, the fluorescence spectrum exhibits excimer bands.

It is not surprising to observe mixed excimer formation between different but similar solecules such as pyrene and its methyl derivatives.^{87,88} Because their electronic transition energies are very close, exciton resonance is still the major contribution to the binding energy of the excimer. Leonhardt and Weller detected an excimertype emission in mixed solutions of two components so dissimilar as perylene and dimethylaniline.⁸⁹ Obviously, the stability of such an exciplex could not result from resonance interaction. Consequently, the emitting species

was interpreted as a charge-transfer complex $A^{-}D^{+}$ which is formed by an electron transfer from the donor D (dimethylaniline) to the acceptor A (perylene) whereas it is unstable in its ground state AD.

Other systems have been studied. The exciplex may occur either by an excited acceptor with an unexcited donor or vice versa.⁹⁰ The typical example follows:

 $A^{*} + D \longrightarrow (A^{-}D^{+})$ A = perylene; D = dimethylaniline $D^{*} + A \longrightarrow (A^{-}D^{+})$ A = 1.4 dioyanobenze; D = pyrene

Usually the component absorbing at longer wavelengths is excited, the reverse is also possible. The exciplex emission can be expressed as follows:^{91,92}

 $(A^{-}D^{+}) \longrightarrow (AD) + hv$

The emission frequency will increase as the ionization potential I of the donor is increased and decrease as the electron affinity, E, of the acceptor is increased. Quantitatively, the relationship can be written as follows:

$$hv = \varepsilon (\overline{A} D^{\dagger}) - \varepsilon (AD) = I(D) - E(A) - C$$

Where C represents the coulomb attraction energy at equilibrium distance. For the same donor, a linear relation is found between the wave number of the band maximum and the electron affinity of the acceptor.

As expected from the electronic structure of exciplexes their emission spectra are solvent dependent. The maximum of fluorescence become red-shifted with increasing solvent polarity. This is paralleled by a strong decrease of the fluorescence quantum yield. Lifetime reflects the combined effects of a decrease in radiative transition probability and an increase in non-radiative transition probability. The former effect⁹³ may result from an increase in heteropolarity of the exciplex in a more polar solvent. The main nonradiative process is the formation of a solvated ion radical pair in competition with exciplex formation.⁹⁴ From the transient absorption and photocurrent measurements, ion radical pair has been demonstrated to occur immediately following electron-transfer and prior to solvent relaxation.

The stability of excimers is explained first by Forster in terms of exciton resonance interaction. The excitation energy has equal distribution over both components $A^*A \leftrightarrow AA^*$. Ferguson later account for excimer stability in terms of change resonance interaction $A^+A \leftrightarrow A^-A^+$. However, from many M.O. calculations, it has become clear that neither the exciton resonance hypothesis nor the charge transfer hypothesis alone is sufficient to explain the stability of the excimer state. Instead, exciton resonance and charge-transfer resonance both contribute to the excimer formation by coupling with equal state representation. This can be described as follows:

$$A^*A \longrightarrow AA^* \longrightarrow A^+A^- \longrightarrow A^-A^+$$

The corresponding wavefunction is:

$$\psi_{exc} = C_1 \{\psi(A^*A) + \psi(AA^*)\} + C_2 \{\psi(A^*A^-) - \psi(A^-A^+)\}$$

where the ratio C_1/C_2 is the relative contribution from exciton and charge-transfer resonance. This ratio may vary from one case to another. But the major term in excimer formation is exciton interaction (C_1) and the major term in exciplex formation is charge transfer interaction (C_2).

B. Luminescence and Absorption Properties of Benzene Derivatives of the Type ϕ - CH₂ - X

The absorption and luminescence properties of model compounds of the type ϕ -(CH₂)-X where X is a substituent have been studied.⁹⁵

It has been shown that the substituent may enhance spin-orbin coupling causing; an increase in intersystem crossing rate constant, fluorescence quenching, phosphorescence-fluorescence ratio enhancement, and a decrease in the natural phosphorescence lifetime. An intramolecular charge-transfer mechanism was proposed which implies that substituted phenylalkyl compounds assume conformations in the ground state whereby the substitutent comes in close contact with the phenyl group.

In such compounds studied, the substitutent in not attached directly to the benzene ring, but through a hydrocarbon chain with one or more methylene groups. The perturbation induced by the substitutent group is therefore therefore much weaker than it is for directly substituted benzene.

The effects produced on a benzene ring by a substituent have been analyzed in terms of inductive and mesomeric effects. The inductive effect is electrostatic and reflects the degree by which the potential field of the substituent perturbs the π electrons of benzene. The mesomeric effect on the other hand involves conjugate interaction, i.e., electronic overlap between the substituent and the benzene It mixes locally excited states with ionic states. ring. These effects may be treated separately if the energy levels of the aromatic group can be adequately described by second order perturbation theory. This is especially true for phenylalkyl compounds where the absorption bands undergo very small shifts. In toluene, the methyl group removes the D_{6h} symmetry of benzene making the ${}^{1}A_{1g} \rightarrow {}^{1}B_{2u}$ transition electric dipole allowed. Thus toluene exhibits two subsystems in its lowest absorption band; namely a vibrationinduced subsystem similar to that of benzene and an electric dipole allowed subsystem. The total oscillator strength of this absorption band in toluence is enhanced relative to that of benzene. Substitution in the methyl group of toluene by an electron-withdrawing group, e.g., COOH, OH, NH₂ decreases its inductive effect. The intensity of the allowed subsystem is decreased markedly in the case of phenylacetic acid and to a lesser extent in benzylalcohol and benzylamine. The oscillator strength of the

 ${}^{1}A_{1g} \longrightarrow {}^{1}B_{2u}$ absorption band is diminished particularly in phenyl-acetic acid where the vibronic structure of the band becomes similar to that of benzene and unlike that of toluene.

McGlynn and co-workers⁹⁶ have shown that charge-transfer states resulting from intermolecular interaction of an electron donor and an electron acceptor molecule produce a decrease in the phsphorescence lifetime, $\tau_{\rm p},$ of the donor molecule and an increase in the phosphorescence-fluorescence quantum yields ratio, ϕ_p/ϕ_F . The dramatic increase in ϕ_p/ϕ_F due to the intermolecular charge-transfer interaction is exemplified by the increase of the quantum yield ratios of acenaphthene by a factor of 75 due to complex formation with symtrinitrobenzene. The increase of ϕ_p/ϕ_F was attributed to an increase in the radiationless intersystem crossing process $S_1 \longrightarrow T$ with rate constant k_{isc} and the radiative triplet process $T \rightarrow S_0$ with rate constant k_p , the latter gives rise to a decrease in τ_p^0 . The decrease in τ_{p} was attributed to both an enhancement of nonradiative triplet decay T $\longrightarrow S_0$ with rate constant k_p ' and an enhancement of radiative triplet decay. The relative importance of these two processes could not be determined in absence of quantum yield measurements.

Relative to toluene the ϕ -CH₂-X compounds exhibit an enhancement of phosphorescence, an increase in ϕ_p/ϕ_F , an increase in k_{isc} particularly at room temperature, and a decrease in the natural phosphorescence lifetime τ_p^0 . The

increase in k manifests itself as fluorescence quenching at room temperature. As mentioned before the decrease in the oscillator strength f of the lowest singlet-singlet transition corresponding to a decrease in the fluorescence rate constant k_r, cannot account for these changes. This strongly suggests that an enhancement in spin-orbit coupling, i.e., mixing of states of different multiplicities, is mainly responsible for the observed changes in luminescent properties. Such changes are similar to those observed as a result of intermolecular charge-transfer interactions mentioned earlier. The proposed mechanism by which spin-orbit coupling is enhanced is an intramolecular charge-transfer interaction where the electron donating and accepting moieties belong to the same molecule. Preliminary studies of the luminescence properties of compounds of the type $\mathtt{Y-\phi-CH}_2-\mathtt{COOH}$ show that the fluorescence quenching increases when the ionization potential of the $y-\phi$ electron donating moiety, Ip, decreases. The decrease in Ip has the effect of decreasing the energy of the charge-transfer state and hence of increasing the mixing of charge-transfer and locally excited states.

Certain absorption bands in the spectra of substituted benzene, ϕ -X, where X is directly linked to the benzene ring, have been assigned as intramolecular charge-transfer transitions. For example, it was suggested that in benzoic acid the 230 nm band contains charge-transfer character; in this case the benzene ring acts as an electron donor and

the substituent as an electron acceptor. In aniline the 235 nm band may also contain CT character; in this case the amino group is the electron donor and the phenyl group the electron acceptor.

The charge-transfer character of the lowest singlet transition of benzoic acid is reflected by the quenching of its fluorescence at 300 and 77°K. The observed and radiative phosphorescence lifetimes of benzoic acid are much shorter than those of toluene, which indicates a large enhancement of intersystem crossing rate constant relative to toluene.

Phenylacetic acid differs from benzoic acid by the presence of a methylene group interposed between the electron donating and accepting moieties. In phenyl-acetic acid the overlap of the electron orbitals of the two groups is only possible for certain molecular conformations where the carboxylic group approaches the benzene ring and for which the orbitals have favorable orientations. In the case of phynylacetic acid such favorable conformations are not negligible, as seen by the marked effects of the carboxylic group on such quantities as k_{isc} and k_p. An extra absorption around 200 nm is observed for phenylacetic acid which presents itself as a shoulder on the ${}^{1}A_{1q} \rightarrow {}^{1}B_{1u}$ absorption. This absorption is not present in the case of toluene and phenylvaleric acid. It could be due to a charge-transfer absorption corresponding to the much more intense absorption at 230 nm of benzoic acid.

When the length of the chain linking the two moieties increases, the number of possible conformations for the molecule becomes very large. Therefore, the statistical weights given to the favorable conformations decrease when the length of the hydrocarbon chain increases. The interaction becomes hardly measurable in the case of phenylvaleric acid.

If spatial approach is required for charge-transfer interaction, steric effects should favor or hinder the electronic overlap between the benzene and the substituent and hence affect the intersystem crossing. Such effects have been observed in the case of 2-phenylbutyric acid which differs from phenylacetic only by an ethyl group attached to the methylene group linking benzene and the substituent. The ethyl group per se has no effect on the emission properties of the benzene as shown by the comparison of the emission properties of toluene and phenylpropane, which have the same fluorescence and phosphorescence yields. However, the ratio of the phosphorescence yield to the fluorescence yield $(\phi_{\rm p}/\phi_{\rm F})$ and the intersystem crossing rate, $k_{\rm isc}$, at 77°K are higher for 2-phenylbutyric acid than for phenylacetic acid. Moreover, the absorption at 220 nm of phenylacetic acid that we ascribed to a charge-transfer absorption is more pronounced with 2-phenylbutyric acid. The absorption and emission properties of 2-phenylbutyric acid show that the ethyl group has an effect on the mutual interaction of the benzene and the substituent in this

molecule. Consideration of molecular models shows that the conformations of 2-phenylbutyric acid for which the benzene and carboxylic groups are close, are favored by the bulky ethyl group.

In molecules such as indan-1-carboxylic acid and indan-2-carboxylic acid, the carboxylic group cannot approach the benzene group because of the five-membered hydrocarbon ring to which it is attached. In these molecules the fluorescence quantum yields at room temperature do not vary with the pH of the solution.⁹⁷ This shows that in the indancarboxylic molecules, intramolecular interactions occurring in chain molecules of the type ϕ -(CH₂)_p-COOH are prevented.

C. Excimer and Charge Transfer Interaction in Diphenylpropane Derivatives

1. Room Temperature Absorption Spectra of Dibenzylether, Dibenzylamine, and Dibenzylsulfide

Comparison of the room temperature absorption spectra of dibenzylether (0), debenzylamine (N), debenzylsulfide (S) with debenzylmethane (c) or diphenylpropane in cyclohexane reveals that a gradual absorption enhancement occurs in the special region corresponding to the first absorption band as shown in Figure 24. This enhancement effect increases in magnitude according to the following order S>N>O>C. The increase in absorption cannot be explained in terms of transition to locally excited state of $(CH_3)_2S$, $(CH_3)_2NH$, $(CH_3)_20$, and C_3H_8 , such conclusion is reached after inspection of the absorption spectra of such



Fig. 24. Room temperature absorption spectra in cyclohexane —— 1.3 diphenylpropane, ···· dibenzylether, —---- dibenzylamine, - - - dibenzylsulfide

compounds. Our alternate interpretation is in terms of a ground state interaction between the heteroatom lone-pair and the aromatic hydrocarbon giving rise to a chargetransfer absorption that accounts for the enhancement effect. The charge-transfer transition that may occur in these benzyl derivatives involve the heteroatom lone pair act as an electron doner and the benzene ring acts as an electron acceptor. One may therefore expect that the energy of the charge transfer state will follow the order of the ionization potential energies of the corresponding dimethyl derivatives. The reported ionization potential of dimethyl sulfide, dimethylamine, dimethylether and propane are 8.68, 8.93, 10, 11.08 ev. 98,99 The intensity of these charge transfer transitions will depend on the extent of electronic overlap of the benzene and heteroatom moieties. One may expect that such overlap will be particular large for the sulphur derivative compound with the nitrogen and oxygen compounds. Thus, the appreciable enhancement observed in the case of dibenzylsulfide compared with dibenzylamine may reflect a more intense charge transfer transition and a lower energy charge transfer band.

A further indication that the intensification effect is due to C.T. absorption comes from studying the effect of adding HCL to ethanolic solution of dibenzylamine. The proton ties the lone pair which is then unaccessible for C.T. interaction. In Figure 25, where the spectra of dibenzylamine in ethanol and in ethanol Hcl media are



Fig. 25. Room temperature absorption spectra of dibenzylamine — in ethanol, -- in ethanol with HCl, $-\cdot--$ in cyclohexane

shown. It is clear that the addition of acid causes the disappearance of C.T. absorption or more preciously the chift of C.T. absorption to higher energies is outside the region of our investigation.

A study of the effect of hydrogen bonding on the absorption spectrum of dibenzylamine provided further evidence. In Figure 25 the absorption spectra of dibenzylamine in cyclohexane and alcohol are compared. The decrease in intensity in alcohol solution is interpreted in terms of a blue shift of the C.T. absorption.

2. Room Temperature Fluorescence Spectra of Dibenzylether, Dibenzylamine and Dibenzylsulfide

Diphenyl propane where two phenyl groups are separated by a saturated hydro carbon chain consisting three carbon atom exhibits excimer emission in cyclohoxane solution at room temperature. The excimer fluorescence has a maximum at 335 nm while the monomer fluorescence with its vibrational structure occur at 285 nm. It is interesting to compare the emission character of Dpp with its analogues where the middle CH_2 group in the carbon chain has been replaced by a heteroatom, i.e., $-\ddot{O}-$, $-N\ddot{H}$, $-\ddot{S}-$. The room temperature emission of these compounds in cyclohexane are compared in Figure 26. Some fluorescence quenching is observed in the case of dibenzylamine, but in the case of dibenzylsulfide remarkable fluorescence quenching occurs. The relative fluorescence intensities are 1 : 0.7 : 0.15 for the 0.N.S. compounds. The order of total fluorescence


Fig. 26. Room temperature emission spectra in cyclohexane; upper--dibenzylehter, middle--dibenzylamine, bottom-dibenzylsulfide

intensity is consistent with the order of absorption enhancement. Our interpretation of this quenching is in terms of a lone pair electron interact with the benzene ring which leads to a C.T. state that has an energy higher than the lowest locally excited singlet state. Mixing such C.T. state with locally excited benzene state leads to an enhancement of intersystem crossing rate and a decrease of the fluorescence intensity.¹⁰⁰

In Figure 26 it is clear that these compounds exhibit a fluorescence band that occur at nearly the same wavelength 335 nm as the diphenylpropane. We interpret this emission as arising from an excimer configuration where the two phenyl groups are parallel to each other. The comparison of fluorescence spectra of dibenzylamine and methyl benzylamine, which with the same concentration, was shown in Figure 27, it clearly indicates the excimer is intramolecular type and not intermolecular type.

The lone pair interaction with the phenyl group in the ground state would favor a configuration as shown in Figure 28. This ground state interaction accounts for the observed absorption enhancement. Mixing locally excited benzene state with C.T. state in which the lone pair acts as an electron doner explains the fluorescence quenching particularly in the sulphur derivative. Excimer formation that occurs in the excited state requires the approach of the two phenge groups and the rotation around the X-c bond where X is the heteratom. Previously it was shown that the



Room temperature emission spectra in cyclohexane: ---- dibenzylamine, ----- methylbenzylamine Fig. 27.



Fig. 28. The conformations of dibenzylamine

activation energy for excimer formation 3.3 to 4.3 Kcal/mole¹⁰¹ in diphenylpropane corresponds to a C-C rotation.

We have studied the room temperature fluorescence spectra of these three compounds in alcohol solution, the results are shown in Figure 29. In the case of dibenzylether, the emission is similar to that in cyclohexane namely a weak monomer band at 290 nm and an excimer band at 340 nm. The small red shift of the excimer band is similar to the red shift observed for diphenylpropane. Its magnitude is 5 nm. In the case of dibenzylamine and dibenzylsulfide the excimer band disappears and instead a broad emission occurs at 405 nm and 455 nm respectively. This obviously does not correspond to excimer fluorescence and could be due to exciplex emission induced by the polar solvent similar to that observed recently in naphtylmethylamine derivatives.¹⁰² To provide concrete evidence for this interpretation, we study the emission and absorption properties of methylbenzylamine -CH2-N-CH3 with dibenzyl-H intramolecular In the former case, no amine. excimer emission is found since it only had one benzene ring.

D. Solvent Induced Intramolecular Exciplex

The absorption spectra of methylbenzylamine and dibenzylamine in cyclohexane are compared in Figure 30. Notice that the CT absorption is more intense in the case





Fig. 30. Room temperature absorption spectra in cyclohexane; ——— methylbenzylamine, — — dibenzylamine

of methylbenzylamine. The room temperature spectra of methylbenzylamine in different solvent are shown in Figure 31. It is clear that in addition to the monomer fluorescence, a broad emission band appears in polar solvents. This band shifts to longer wavelength as the polarity of the medium is increased. In hydrocarbon solvent this band is absent and is highly polar solvent such as H₂O, the fluorescence intensity is small.

The geometric requirement for intramolecular exciplex interaction between an aliphatic amine and an aromatic hydrocarbon are expected to be less restrictive compared with the case of intramolecular excimer of diarylalkanes. In the latter cases, the exciton interaction is the major contributor to the binding energy of excimer which the two aryl moieties must strongly overlap in a sandwich way. In the exciplex case, the major contribution to the binding energy is due to the change resonance interaction.

J.A. Ibemisi, M.A. El-Bayoumi, and J. Kinsinger¹⁰² has reported the solvent induced exciplex fluorescence of β -naphthyl-methylamine. The dependence of the exciplex fluorescence maximum and its intensity on the polarity of the medium has been studied.

From the study of emission of methyl benzylamine in various solvents, the plotting of $\Delta\delta$ with respect to $\frac{2(\epsilon-1)}{2\epsilon+1} = \frac{2(n^2-1)}{2n^2+1}$ is a straight line (see Figure 32).







From its slope, $\Delta\mu$ can be estimated, about 8 Debye, which is close to the value for most exciplex which has been published. The other two compounds benzylamine, dibenzylamine, do have weaker charge transfer interaction from the study of absorption spectrum, but no exciplex has been observed in the emission spectrum. It could be either the basicity is weaker so that the charge transfer fluorescence state never is below the L_b state and the steric effect prevents the exciplex formation.

It is interesting to study fluorescence change resulting from the addition of HCl in the ethanol solution of dibenzylamine. Figure 33 shows that small quantity of acid lead to a gradual disappearance of the exciplex emission at 410 nm and the gradual enhancement of excimer emission at 355 nm. Further addition of acid leads to a gradual enhancement of the excimer emission. The emission of the protonated dibenzylamine is similar to that of diphenylpropane (see Figure 34).

It is interesting to observe that as the excitation wavelength change from 265 nm to 255 nm, the fluorescence spectra of dibenzylamine in chclohexane exhibit small change. When we excite in the neighborhood of the CT absorption 255 nm, the ratio of excimer to monomer emission is enhanced. It appears that in solution there is more than one conformation besides the conformation shown in Figure 28, where the lone pair electron interact with the phenyl group. There are other conformations where such interaction



Fig. 33. Room temperature emission of dibenzylamine in ethanol number means the amount of adding HCl(0.25N in ul unit)



Fig. 34. Room temperature emission of dibenzylamine in ethanol (bottom line), in presence excess HCl (upper)

methylbenzylamine	
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(max)	
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JUEATOS	ω	ц.	v max	E	с т (Мах.)	4	
Cyclohexane	2.0	1.4266				0.9744	
ata.3	4.8	1.4 459				0.2532	
CH2 CH2	9.8	1.4242	27248	367	0.1666	0.3255	11512
n-butanol	17.8	1.3993	24289	4117	0.3616	0.3616	14470
Ethanol	24.3	1.3611	23696	422	0.5965	0.37915	15063
Methanol	33.0	1.3288	23094	433	0.2388	0.3931	15665
H ₂ 0	78.54	1.3384	22075	453	0.098	0.4044	16684

 $\varepsilon = dielectric const.; \quad \Delta \delta = stoke shift; n = reflection index$

does not occur or are weaker. One should realize that the binding energy due to CT interaction is small.

It has been well established that the longer wavelength emission observed in diphenylpropane corresponds to intramolecular excimer. A comparison of the emission of methylbenzylamine and dibenzylamine at same concentration in cyclohexane shown in Figure 30 establize clearly that the phenomenon that we observe is intramolecular excimer.

One may summarize the various process that may occur as a result of excitation of dibenaylamine as follows:

- 1. Configurations in which the lone pair interact in ground state with phenyl group may give rise to
 - a. excimer emission at 350 nm. This require rotation around C-C to bring about the two phenyl ring in parallel conformation (Step 1).
 - b. exciplex emission if the solvent is polar enough to stabilize the CT state below the ${}^{1}L_{b}$ state; in ethanol this emission occurs at 410 nm the emission wavelength and intensity are both solvent dependent (Step 2).
- Conformation where no or very weak interactions may occur between lone pair and benzene ring lead to monomer emission (290 nm) (Step 3).
- 3. If decay occurs to the triplet state and the medium is rigid Step 3 and 2 may occur in triplet state leading



Fig. 35. Room temperature emission of dibenzylamine in cyclohexane with different excitation wavelength; curve 1--265 nm; curve 2--260 nm, curve 3--255 nm



Fig. 36. The kinetic scheme for excited dibenzylamine of its relatives

to monomer phosphorescence, exciplex phosphorescence excimer phosphorescence respectively.

E. Triplet Excimer Formation in Dibenzyl Derivatives

A molecule in its triplet state $({}^{3}M^{*})$ may form a stable stiplet excimer $({}^{3}D)$ with a molecule in its ground singlet state $({}^{1}M)$:

 $^{1}M + ^{3}M^{*} \rightarrow ^{3}E$

One would expect that triplet excimer formation will give rise to an additional component in the phosphorescence spectrum which is red shifted with respect to the monomer phosphorescence. Broad phosphorescence band systems having their intensity maxima about 5000 cm⁻¹ lower in energy than the 0,0 monomer phosphorescence have been observed in the case of halogenated benzene crystals at low temperatures.⁹⁷ In these crystals translationally equivalent molecules are spaced closely among one crystal axis such that excimertype interaction is possible.

The red shift ($\approx 1000 \text{ cm}^{-1}$) of the phosphorescence spectrum of (4.4) paracyclophane in EPA at 77°K has been attributed⁹⁸ to triplet excimer interaction. In this molecule the two benzene rings are held together by methylene bridges in a sandwich structure with an interring separation of ≈ 3.5 A. Emission bands are observed at $\approx 20000 \text{ cm}^{-1}$ in liquid alkyl benzenes as a result of intense electron beam excitation. These emissions were attributed to excimer phosphorescence produced by ionrecombination processes. Solid benzene at 138°K excited by 1MeV electron beam exhibits a phosphorescence spectrum which in addition to the monomer phosphorescence has a structureless component beyond 430 nm, the latter has been attributed to an emission from a "triplet charge-exchange excimer."

The emission observed from a 10^{-3} M degassed solution of diphenylpropane in 3MP at 77°K is recorded after the sample was allowed to warm up slightly. The estimated temperature is about 115°K. The phosphorescence spectrum in the latter case is shifted to longer wavelengths with a maximum at 420 nm. When the sample was allowed to further warm up and the viscosity of the solution decreased the intensity of phosphorescence decreased rapidly until it was completely quenched and only monomer fluorescence is emitted. At such viscosities diffusional relaxation leading to singlet excimer formation during the lifetime of the excited monomer singlet state does not occur. Excimer fluorescence at 330 nm began to appear and dominated the specstra in the neighborhood of room temperature at appreciably lower viscosity. The 420 nm emission was interpreted as excimer phosphorescence.

The low temperature and high viscosity will prevent the triplet state from the quenching by O₂ and solvent molecules, but the fast difussion of the chromophore within the lifetime of its triplet is the initial requirement for triplet excimer formation, therefore, very few triplet excimer has been found. The other reason for sear observing the triplet excimer is its unstability relative to singlet excimer; only charge transfer resonance contribute to the binding of triplet excimer. The triplet excimer has been found in trihalogenbenzene crystal, but not in benzene crystal itself. This may be explained in terms of increasing the intersystem crossing rate due to the heavy atom effect.

The phosphorescence of dibenzylether, dibenzylamine and dibenzylsulfide have been measured in EPA at 77°K are shown in Figure 37. The spectra seems to have two components, one with a maximum at 380 nm corresponding to the emission of toluene at 77°K, the other with a maximum at 425 nm, for the (S) compound, its phosphorescence seems totally belong to the second component.

The total emission spectra of dibenzylamine and toluene in EPA at 77°K are compared in Figure 38. The 280 m band is the fluorescence band corresponding to the toluene moiety and the broad phosphorescence band between 330 nm and 600 nm exhibits two types of fine structure. Vibronic bands near 380 nm have phosphorescence lifetime of 4.5 sec while bands at longer wavelength (e.g., at 425 nm) exhibit a short lifetime of around 0.6 sec.

Phosphorescence bands at 400, 420, 440 nm are similar to the triplet excimer emission from tribromobenzene crystal. To determine whether that emission is an



Fig. 37. The phosphorescence in E.P.A.; upper--dibenzylsulfide, middle--dibenzylether, bottom--dibenzylamine



intermolecular or intra molecular excimer phosphorescence or exciplex phosphorescence. The emission of methylbenzylamine in EPA was measured. The phosphorescence spectrum shows only the toluene type phosphorescence (see Figure 39), therefore, the phosphorescence bands in the 425 nm region could correspond to the intramolecular triplet excimer in the dibenzylamine. A similar phenomenon was observed in dibenzylether. The lifetime data was shown in Figure 40.







Fig. 40. The decay curve of MBA in glass (A) The decay curve of phosphorescence of DBA in glass (B); upper--emission wavelength 380 nm, middle--emission wavelength 420 nm, bottom--emission wavelength 450 nm

CHAPTER IV

BIOLOGICAL APPLICATION OF FLUORESCENCE PROBE

Fluorescence techniques have been used to investigate macromolecules in which the lifetime of the excited state is sufficiently long for a variety of thermal and physical processes to take place prior to emission. These processes include proton transfer, intramolecular excimer formation, exciplex formation, solvent cage interaction, and intramolecular twisting relaxation. Dramatic changes in the luminescence properties often occur as a result of these processes, e.g., large stokes shift, appearance of a new fluorescence band, significant fluorescence intensity change and/or fluorescence lifetime different from those calculated from absorption intensities.⁹⁹ All these phenomena are very sensitive to the characteristics of the solvent, e.g., its polarity, proton-donating or accepting character, and its viscosity.¹⁰⁰⁻¹⁰⁵

Therefore, those series of fluorescence compound under large relaxation in the excited state can be used as probes to attach to the biological system by noncovalent bond. From the measurement of emission, the static and dynamic environment of fluorescence probe will be known, and therefore becomes a very useful tool to study the polarity and

mobility in the binding site of biomacromolecules and also tell us the dynamic conformation change in some enzyme reaction.

A. Proton Transfer and Biological Application

The first example of a proton transfer, probe is an Aromatic alcohol which has been used as an extrinsic probe 106,107, to investigate the proton-accepting character of the immediate environment at chromophore binding sites. It is well known that the pKa of aromatic alcohols is lower in the excited state than in the ground state. The pKa for naphthol is 9.8 in the ground state but about 2 in the excited state.¹⁰⁸ At neutral pH, the absorption will be due to the protonated species and in the excited state, equilibrium will favor the formation of deprotonated species. Emission can be observed due to the protonated species, the deprotonated species, or both, depending on the rate of proton transfer. If the rate of proton transfer is of the same order of magnitude as the rate of the fluorescence decay, the proton transfer process can be visualized directly by means of nanosecond time-resolved emission spectroscopy. 109

The rate of an excited state proton transfer of α -naphthol 6-sulfonate in aqueous solution is fact, such that the predominant emission is at 425 nm, due to the ionized species. However, when it complexes with bovine serum albumin, the predominant emission is then at 350 nm, due to the protonated species. This indicates a significant decrease in the rate of proton transfer when the probe is associated with the protein.¹⁰⁷ A similar result was obtained with dehydroluciferin, which showed rapid rates of excited state proton transfer in aqueous solution but a slow rate when absorbed to the active site fluciferin.

Tyrosine, an intrinsic probe, might also be valuable since it is known to undergo excited state proton transfer.^{110, 111} This method then provides a new, quantitative application of fluorescence in the study of biological systems.

The compounds which we used to study the proton transfer are 7-azaindole and α -carboline. Both of these compounds can form the double hydrogen bond with another molecule which has a pair of close and basic group. The rate of proton transfer can be estimated easily by measurin the ratio of amount of F_2 band from the deprotenated species to F_1 band (from the protonated species; this depends upon the type of hydrogen bond).

B. Charge Transfer and Biological Application

The molecule with charge transfer interaction is the most useful fluorescence probe. Since the maximum of emission bands, the quantum yield of emission and the lifetime of fluorescence are changed dramatically from polar solvent to nonpolar solvent. Three kinds of properties make them become the most useful tool in studying the

polarity character of the binding site in the enzyme.

Weber & Laurence first described the dramatic observation that while only weak green fluorescence was emitted when ANS dyes were dissolved in aqueous solutions, intense blue fluorescence occurred when the chromophores absorbed to bovine serum albumin.¹¹² This intense blue fluorescence was also observed in nonpolar organic solvents which became known as "hydrophobic probes." The subsequent finding by Stryer that these dyes absorbed specifically to the heme binding site in apomyoglobin and apohemoglobin initiated many investigations related to their interaction with protein membranes, subcellular particles, and cells.¹¹³ In addition, many other aimilar probes such as TNS (toluidinonaphthalene-6 sulfonate)¹¹⁴⁻¹¹⁶ also have been used in the biological system. Its fluorescence is even more sensitive than that of ANS.

Charge transfer probe that are sensitive to solvent environment may exhibit a red shift of fluorescence maximum, a broadening of fluorescence band as well as a decrease in fluorescence intensity as the polarity of the solvent increase. Methylbenzyeamine can serve as a charge transfer probe. It exhibits solvent-induced exciplex formation. In my study, I discovered the more polar the solvent, the greater the red shift and the less the quantum yield. It could be utilized as a new fluorescence probe to study the local polar environment of biomacromolecules.

C. Excimer-Exciplex and Biological Application

A membrane is an oriented, two dimensional, viscous solution of amphipathic proteins and lipids. Its instantaneous thermodynamic equilibrium leads to many functions such as nerve impulse transmission, membrane transportanes, ¹³⁰ and drug interaction.

In recent years, a number of new concepts have developed, for example, no longer is a biological membrane considered a static mixture to rigidly fixed components, but rather a dynamic mosaic of molecules which undergo various types and degrees of motion.¹¹⁷ Phospolipid molecules have been shown to undergo rapid lateral diffusion¹¹⁸ within the plane of a membrane and even slow transverse diffusion across that plane.¹¹⁹ While lipids were once viewed as simply a matrix in which proteins existed and functioned autonomously, recent evidence indicates that proteins interact strongly with boundary lipids which controls the activation energy of enzyme function.

The influence of this type of non-rigidity of the mosaic structure can be stated in general form as follows: "The physical or chemical perturbation of a membrane may affect or alter a particular membrane component or set of components; a redistribution of membrane components can then occur by translational diffusion through the fiscous two-dimensional solution, thereby allowing new thermodynamic interactions. Among the altered components to take effect, this general mechanism plays an important role in various

membrane mediated cellular phenomena."120

The kind of nonrigidity or fluidity of membranes will also depend on the structure of its component proteins, lipids and the interactions that occur between them. It can be detected by ESR probe 121,122 and fluorescence probe. Since the excimer formation is viscosity dependent, it can be used as the fluorescence probe to detect the rigidity of membranes. Pyrene is the first can be used because its excimer is stable and intense and can be detected easily. The more fluid the membrane is, the more intense the excimer fluorescence is, therefore the ration of excimer emission to the monomer emission of pyrene becomes a rule to estimate the fluidity of membranes¹²³ which control the activation energy of enzyme behavior such as the activity of NADH oxidase, D-lactate oxidase.¹²⁴ Intramolecular excimer formation in contrast to intermolecular excimer formation (pyrene) is not concentration dependent. The benefit of the much lower concentration requirement for intramolecular excimer formation makes it become a more suitable probe for various membranes, including the more rigid membrane which can't be detected by intermolecular excimer formation by long range diffusion.

CHAPTER V

EXPERIMENTAL

A. Preparation of Chemical Compounds

1. α -Carboline

 α -carboline was synthesized by using the method of L. Stephensen¹²⁵ and W.K. Warburton, and recrystallized from ethanol several times. Confirmation of the identity of the compound was done by measuring the melting point 217°c and obtaining the mass spectrum. The pyrrolic hydrogen was identified by N.M.R. with $\tau = -1.79$. The U.V. absorption spectrum is almost identical to that of carbazole. The expected $n+\pi^*$ transition must be completely covered by the more intense $n+\pi^*$ absorption band.

2. N_1 -methyl α -carboline Tautomer

After dissolving 1 gm of carboline in toluene, we add 1.5 ml dimethylsulphate. The solution was refluxed for 10 hours, then cooled down, filtered, and recrystallized from acetone and methanol. The white crystal has been identified as α -carbolium methylsulphate. After dissolving in acetone, it was neutralized by adding NaOH solution. The yellow precipate is separated by alumina column. The final bright yellow crystal with M.P. 130 to 132°C has been identified as N₁-methyl α -carboline

tautomer by Mass, N.M.R., U.V., spectra.

3. No methyl α -carboline

 N_9 methyl α -carboline was synthesized using a procedure similar to that used by Robison¹²⁶ for the synthesis of 7-methyl 7H₁ pyrrolo (2,3-b) pyridine.

4. N_{q} -D- α -carboline

The α -carboline was dissolved in the THF (tetra hydro faran). After adding NaCD/D₂O solution, it refluxed for two hours. The white crystal will be obtained after evaporating the THF. The Mass spectrum shows that 90% of α -carboline is deuterated and its absorption spectrum and emission spectrum is identical to that of α -carboline at room temperature.

5. Benzyl Derivatives

The dibenzyl amine, methyl benzyl amine, benzyl amine, methyl benzyl ether, methyl benzyl sulfide are obtained from the Aldrich chemical company. The dibenzyl ether is obtained from the Chemical Procurement Laboratory. All of them have been distilled under reduced pressure for three times. The dibenzyl sulfide is from the Chemical Procurement Laboratory and recrystallized from ethanol three times.

B. Purification of Solvents

1. 3-methylpentane

The Phillips pure grade 3-methylpentane was mixed with nitric acid and sulfuric acid, then stirred for two days. Then it was separated and washed with base and water. After drying with sodium sulfate for two days, the solution was refluxed over sodium wire for 48 hours and distilled. The vapor passed through a four foot vacuum jacketed column and condensed at a speed of two drops per minute. The purity was checked by obtaining the absorption spectrum.

2. Ethanol

200 proof ethanol was distilled through a 1 meter vacuum jacket column. The distillation rate was adjusted such that a very slow rate (about 5 drops per minute) was maintained. Distillation continued until the benzenealcohol azeotrope was no longer present as determined by an absorption spectrum of the distilled alcohol in a 10 cm cell. That is, the characteristic benzene UV absorption was no longer apparent. Ethanol was then distilled and used as needed.

3. Deuterium Oxide

99.81 atom %, 0.2 uc Tritium/ml. International Chemical and Nuclear Corporation (ICN).

4. Ethyl Alcohol-d

99% Aldrich Chemical Company.

5. Cyclohexane

Aldrich Chemical Company (spectra grade).

C. Spectral Measurement

1. Absorption Spectra

All of the absorption spectra were run on a Cary 15 and Cary 17 spectro-photometer in room temperature or liquid nitrogen temperature.

2. Emission Spectra

Most of the fluorescence spectra were run on an Amico spectro fluorimeter which is equipped with high pressure Xenon lamp and EMI 9781 R photomuliplier tube.

To obtain better resolved emission spectra, a spex set up was used. A high intensity Xenon lamp was used as the light source, the excitation wavelengths were selected using a Bausch & Lamb monochrometer which has a grating of 500 mm. The excitation light was focuses on the sample using a quartz lense. We placed the right angle of the sample cell a high resolution spex 1700 - I monochrometer with an EMI 9558 QA photomultiplier tube that can be cooled. The power supply of the pm tube is Fluke 412B, operated at 1100 V. The signal to noise ratio is enhanced using a PAR HR-8, lock-in amplifier. The reference signal is from the photodiode in the chopper which is located in between the incident monochrometer and the sample.

The phosphorescence spectra were obtained using the Amico fluorimeter and a mechanical two window chopper, whose speed can be varied. The measurement of phosphorescence lifetime depends on the lifetime range. If it

is in the several second range, a shutter that cuts the exciting light was used. If the lifetime is in the tenths of second range, we used a specially designed shutter with speeds in the msec range. The data are projected on a one sweep storage oscilloscope and taken by a polaroid camera.

3. Degassing Samples

Some of the sample has to be degassed before luminscence measurements. After cooling with liquid nitrogen, the sample cell is attached to high vacuum line. It has to be evacuated by the mechanical pump first, then the oil diffusion pump, until the pressure drops to 10^{-6} torr, closing the stopcock, allowing the sample to thaw, refreezing, evacuating the tube and continuing this freeze-thaw cycling until the vacuum line ionization gauge did not quiver when the stopcock was opened after a freeze.

4. Quantum Yield

The quantum yield of α -carboline can be estimated by comparing its fluorescence intensity with that of carbazole since their emission in the same range and the quantum yield of carbazole is known.

Suppose N_1 and N_2 photons were measured respectively, the ratio of quantum yield will be N_1/N_2 . In some cases, their emission bands are in different ranges. The correction for the PM response in different wavelengths becomes necessary. In comparison of the quantum yield of two compounds which are separately dissolved in different
solvents, it is necessary to consider the reflection index of the solvent, since it will broaden the angle of aperture of the incident light by n^2 . Suppose n_1 and n_2 are refraction index of solvent 1 and solvent 2. The ratio of quantum yield will be:

$$\frac{\phi_2}{\phi_1} = \frac{N_2(n_2)^2}{N_1(n_1)^2}$$

If the quantum yield should be determined at 77°K, one should consider the solvent contraction by cooling since it causes the increasing of the local concentration and changes the refraction index.

5. The Corrected Excitation Spectrum

Excitation spectra were obtained by setting the emission monochromator at a certain wavelength and scan the excitation wavelength. Excitation spectrum must be corrected to compensate for the intensity variation of the different excitation wavelength.

Suppose the photomultiplier output P is directly proportional to the total flux Q of the fluorescence emitted by a given species:

$$P = KQ = KI_{O}$$
 (2.3 ε cl) ϕ_{f}

Where K is an instrumental constant, therefore, for a solution with given concentration: PαIcεφ_f

 I_{o} is the intensity of the lamp. The value of P is not only dependent upon the properties of the solute molecules but also on the character of the lamp itself.

The way to cancel out I_0 is by using a beam splitter after the incident monochrometer and before the sample cell and by taking the ratio of the two responses from the two photomultipliers. A_2/A_1 , A_2 is for sample, A_1 is for reference. The system which we used is computer interfaced set up designed by Holland.²¹⁹ The corrected excitation spectrum is printed out automatically.

6. Temperature Variation System

A quartz dewar with a flat quartz excitation window and all cm square suprasil cuvette were used. The temperature of the sample was controlled by boiling liquid nitrogen using a power resistor and allowing the N_2 gas to flow into the sample dewar. The temperature of the sample was monitored through a thermocouple (copper, constantan) attached to the outside of the cuvette immediately above the point of excitation. Comparing readings of thermocouple on the outside and inside of a cuvette containing solvent, one finds not more than 1° difference between thermocouples over wide ranges of temperature. The lowest stable temperature which can be reached in such a system is around -200° C.

7. Fluorescence Decay Curves

For the measurement of fluorescence lifetime, a single photon counting technique is used. This is because it has the highest sensitivity, reliability, beside commercial availability for most of its components. The major parts of the apparatus are, the nanosecond flash lamp with band width around 2 nsec, a single photon counting photomultiplier DUVP 56 with a high gain, the time amplitude converter with an automatic sweep after starting, and a multichannel analyzer with the capacity to arrange the signals to different channels according to their pulse height (see Figure 42).

There are two types of flash lamp, usually used. One is the free run lamp. It is easy to operate and construct, but it lacks any flexibility in operations. The second type, which we used is called a gated lamp. The added capacitance can be changed to any desired voltage within the capability of the thyratron which is used for gating the lamp to ground. The repetition rate is controlled only by the pulse rate of the thyrator and it is essentially independent of the nature of the gas or pressure. The usual rate of flash is between 5Kc and 15Kc. The frequency of the flash can be detected by 1P28 phototube. The resulting signal after discriminator initiates the T.A.C. time sweep.

Fluorescence photons are detected by a fast photomultiplier 56 DUVP (Time resolution 800 picoseconds). This

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Fig. 41. Block diagram of time resolved spectrophotometer



Fig. 42. The idea of time-to-amplitude converter

tube is capable of amplifying a single photon into an electrical pulse of several volts. This pulse is used to stop the TAC time sweep.

The time resolution of the apparatus depends upon the uncertainty of timing the detection of single-photon pulses relative to the flashlamp pulse. The principal time jitter arises from the fact that the amplitude of single-photon pulses is not constant but covers a broad range in pulse heights. The jitter associated with timing by single-level crossing was eliminated by using a "constant fraction timing" discriminator (ORTEC Model 463). In this type of instrument the input pulse is split into two channels; one channel is inverted and delayed and the other channel is simply attenuated. The channels are added such that the resultant bipolar pulse has the desired fractional trigger threshold associated with its zero crossing point. This effectively eliminates the time jitter.

The most important part of the instrument is the T.A.C., the operation of which is illustrated in Figure 32. Each time the lamp flashes, a synchronization pulse from lp28 will initiate TAC time sweep and a stop pulse is received from the DUVP56 by accepting a single proton during the time sweep. The output of T.A.C. is generated with amplitude proportional to the time $(t_{stop} - t_{start})$, and recognized by M.C.A. (multi-channel analyzer) and arranged into appropriate channel. The slower the signal, the smaller the amplitude, the smaller the channel number

it is stored. As the time passes, the information in these channels is accumulated and is displayed on an oscilloscope. For my experiment, the time interval for each channel is 0.0383 nsec, which can be adjusted by changing the bias in T.A.C. The accumulated data can also be fed into a teletype and punched out on paper tape. By using an acoustic couple and teletype, the paper tape can be read into CDC 6500 computer where the deconvolution will proceed. The information afger deconvolution will be sent back and plotted on a three log paper.

The reason for deconvolution is that we can't consider the lamp curve as a function anymore, because the fluorescence decay phenomenon which we are concerned is in nsec range, therefore, the output of T.A.C. will contain the lamp shape factor. The way to take off the lamp factor is called deconvolution. The detailed mathematics for deconvolution is as follows:

Suppose the observed curve is I_F^{obs} (t)

$$I_{F}^{obs}(t) = \int_{0}^{t} G(t') F(t - t') dt'$$

G(t) is the true decay function of fluorescence F(t) is the lamp curve

There are several methods for getting G(t) from I_f and F(t). The comparison of these methods has been reviewed by W.R. Ware. In our lab, we used the deconvolution procedure suggested by Ware. According to his procedure, G(t) is expressed as:

$$G(t) = \sum_{k=1}^{n} a_k \exp(-t/r_k)$$

Where Y_k has a fixed value, can be selected by the experience and intuition about the lifetime of detected systems. The least square fitting are used to obtain the best weith factor in order to get the smallest residue between the observed decay curve and the calculated decay curve:

$$I^{cal}(ti) = \int_{0}^{ti} \sum_{k} a_{k} \exp(-ti/r_{k}) F(t-t) dt'$$

The residual P_i and for the ith data point (ith channel) is given by

$$\rho_{i} = I_{F}^{obs} (t_{i}) - I_{F}^{cal} (t_{i})$$

The deconvolution problem then reduces to obtaining the coefficients a_k such that

$$\sum_{i} \rho_{i} d \rho_{i} / d a_{j} = 0 \qquad j = 1, 2... "$$

Time resolved spectra were obtained by measuring the emission spectrum within a time window, which can be done by selecting only one channel analyzer following the T.A.C. If we fixed time between t and t + Δ t, after the lamp discharges and changes the fluorescence wavelength, it will give the time-resolved fluorescence spectrum from the duration between t and t + Δ t.

In advance, the multichannel pulse high analyzer still can be used in its multichannel scaling mode, but the number of channel represents the wavelength and not the time anymore. For the higher optical resolution, the 1024 channels would be used instead of the 128 channel in the normal case. It will give the better resolution in the treatment of multicomponent decay problem.

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