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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF A FLUORESCENT POLYAMIDE SERIES AND THEIR MONOMER ANALOGS: NOVEL INTRA-MOLECULAR EXCIMER AND EXCIPLEX INTERACTIONS

Bу

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ABSTRACT

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF A FLUORESCENT POLYAMIDE SERIES AND THEIR MONOMER ANALOGS: NOVEL INTRAMOLECULAR EXCIMER AND EXCIPLEX INTERACTIONS

By

John Akolisa Ibemesi

The photophysical properties of a fluorescent aromatic polyamide-series and their monomer analogs have been utilized to investigate:

i) the configurational and conformational requirements for intramolecular excimer formation in hetero-chain polymeric systems.

ii) The effect of chain-binding on the reactivity of a chemical moiety.

iii) The mechanism of solvent-induced intramolecular exciplex fluorescence in aromatic hydrocarbon-aliphatic amine systems; and

iv) The nature of exciplex interaction with polar molecules.

The series of polyamides was synthesized from 2,6-Bis(N-methyl, methylamino)naphthalene and the diacid chlorides, $Cl-C+CH_2+C-Cl$ (n=2, 4, 6 and 8) by interfacial polycondensation. These polyamides, designated as P-2, P-4, P-6 and P-8, possess widely-separated, doubly-bonded naphthyl groups in the back-bone. They were characterized as having flexible, amorphous chains, and with good solubility properties. Their molecular weight was estimated to be 20,000.

The monomer analogs: 2,6-Bis(methylamino)naphthalene (II), 2,6-Bis(N-methyl, methylamino)naphthalene (III) and 2,6-Bis(N-dimethyl, methylamino)naphthalene (IV), were synthesized by reacting 2,6-Bis(bromomethyl)naphthalene with ammonia, methylamine and dimethyl amine respectively. The model compound, 2,6-Bis(N-methyl, N-acetyl, methylamino)naphthalene (MC) was obtained by acetylation of III.

The room temperature absorption and emission spectra of dilute solutions of P-2, P-4, P-6 and P-8 were measured. Their emission spectra showed the formation of intramolecular excimers between naphthyl groups separated from one another by as many as 20, 2N and 10C atoms. The fluorescence lifetimes and quantum yields were dependent on the distance of separation between the chromophores, in a manner that appeared to involve non-neighboring naphthyl groups in excimeric interactions. Temperature measurements revealed a small energy requirement for the conformational transitions involved in the formation of these excimers. Dimer fluorescence was detected at high polymer concentrations. Addition of small amounts of triethylamine (quencher) to dilute solutions of the polyamides and the model compound, led to the quenching of monomer (naphthalene) fluorescence and the formation of intermolecular exciplex. A kinetic analysis of monomer fluorescence quenching was done, which considered the formation of fluorescent exciplex and a transitory non-fluorescent charge-transfer (CT) complex. A plot of the ratio of intensities of exciplex and monomer emissions, I_E/I_M , as a function of quencher concentration, showed the model compound to be more reactive than the polyamides; and among the polymers, the order of reactivity is P-8 > P-6 \approx P-4 > P-2. Thus, chainbinding and chain rigidity appear to have decreased the reactivity of a chromophore.

The room temperature absorption and emission spectra of compounds II, III and IV were measured in solvents of different polarities. All three compounds exhibited intramolecular exciplex fluorescence <u>only</u> in polar solvents, with intensity in the order: IV > III >> II. In nonpolar solvents, substantial quenching of monomer fluorescence occurred; this was attributed to a charge-transferinduced intersystem crossing enhancement. Evidence for this quenching mechanism was obtained from the total emission properties of II, III and IV at 77°K, relative to those of 2,6-dimethylnaphthalene. Quenching of exciplex fluorescence in II, III and IV by water showed 'static' quenching to be predominant, and appeared to reflect the specificity of the interaction of exciplex with protic solvents.

The case of non-protic polar solvents was investigated by adding small amounts of methyl cyanide (MeCN), N,Ndimethylformamide (DMF), dimethylsulfoxide (DMSO) and hexamethylphosphoramide (HMPA) to dilute solutions of IV in ether and methylcyclohexane (MCH). In ether, red-shifts in exciplex emission maxima were observed, which appeared to indicate the involvement of both specific interaction and dielectric effect. The former was considered to arise from the nucleophilic property (donicity) of the polar species; while the latter was attributed to aggregation of polar species in a non-polar medium. The emergence and growth of exciplex fluorescence of IV in MCH at low concentrations of added polar species was considered further evidence of the specificity of the interaction of an excited dipolar species (e.g., exciplex) with surrounding dipolar molecules.

То

My Mother

(for pioneering my early education)

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CHAPTER 1

INTRODUCTION

Definition

The chemical characters in this scientific "drama" (dissertation) are called excimers and exciplexes. These are defined as: "transient atomic or molecular complexes, with associated excited electronic states, dissociative ground states and structureless emission spectra." Their formation can be illustrated as follows:



Thus, an encounter between an excited chemical moiety, A^{*} and an identical or different ground state species leads to an excimer or exciplex respectively. In general, a singlet or triplet excited complex can be formed, depending on the spin state of A^{*}. The spectral characteristics of these complexes, implicit in the above definition, are depicted in Figure 1.1, which is a potential energy diagram



Figure 1.1. Potential Energy Diagram for Excimer Formation.¹

for the case of excimer formation.¹ The excimer emission, $h\nu_e^{\circ}$ is structureless because its ground state is repulsive (dissociative) while the monomer emission, $h\nu_m^{\circ}$ is structured because of electronic transitions to various vibrational levels.

Historical

The phenomenon of excimer formation was first discovered by Lord Rayleigh² (1927) when he observed in the ultraviolet emission spectra of high-pressure mercury vapor, a broad continuum, superimposed on the partially quenched atomic line spectrum. The continuous emission was attributed to the excited triplet excimer of mercury - ${}^{3}\text{Hg}_{2}^{**}$. Thereafter (1930), Hopfield³ observed the first singlet excimer emission from an excited helium dimer - He^{*}₂. Other noble gases behave similarly; in fact, the ultraviolet emission continuum from a high-pressure Xenon (Xe) lamp (a widely used light source in optical spectroscopy) originates from the xenon excimer Xe^{*}₂.

For a while, excimer formation remained an event observable only in the gaseous phase of atomic systems. This situation was drastically altered in 1954 when Förster and Kasper,^{4,5} working with pyrene solutions, observed that, as the solution concentration increased, a decrease in the structured molecular fluorescence of pyrene occurred, followed by the appearance of a broad-structureless band

at lower energies than the quenched molecular fluorescence. Since the absorption spectra of concentrated pyrene solutions showed no new band, they attributed the above-mentioned "anomalous" fluorescence to emission from an excited dimeric pyrene complex produced by the association of one singlet excited molecule and one singlet ground state molecule. A few years later (1958), similar observations were reported for 9-alkylanthracenes⁶ and for 2,5-diphenyloxazole.⁷ The break-through came in 1962 with benzene and naphthalene⁸⁻¹⁰ followed by a host of other arcmatic hydrocarbons and their derivatives^{11,12}Thus, within a decade, excimer fluorescence in fluid solutions of aromatic systems was established, from an exception, to a common observance. Similar observations have been made in other condensed-phases of aromatic molecules such as in pure liquids and molecular crystals.^{13,14}

Another milestone in the discovery of excimers occurred in 1965 when Hirayama¹⁵ published the first reports on intramolecular excimers in diphenyl and triphenyl alkanes; this was closely followed by the paper on paracyclophanes and vinyl polymers by Vala, et al.¹⁶ Earlier, in 1962, Basile¹⁷ had published the first fluorescence spectrum of pure polystyrene; and in 1963, the first suggestion of excimer formation (intramolecular) in dilute solution of isotactic polystyrene was made by Yanari et al.¹⁸ By binding the two interacting aromatic groups in the same molecule by means of a molecular chain, the probability of their encountering

each other within the life time of the excited state becomes enhanced; thus, even in very dilute solutions, intra-molecular excimer fluorescence is observable.

The history of exciplexes started in 1963 in an investigation by Leonhardt and Weller¹⁹ of the fluorescence quenching of perylene by typical electron donors (D) like anilines. They observed a broad, structureless emission band about 5000 cm^{-1} to the red of the normal structured fluorescence of the aromatic hydrocarbon (A). The new fluorescence increased in intensity with increasing donor concentration, at the expense of perylene fluorescence, while the absorption spectra remained unchanged. They therefore attributed the anomalous emission to an excited molecular complex species $(\overline{A} - D^+)$, which was stable in the excited state but unstable in the ground state. Such a complex, sometimes called "heteroexcimer" has been observed in numerous donor-acceptor systems. 20-23 The intramolecular case was first reported by Chandross and Thomas (1971)²⁴ in naphthylalkylamines.

There is another class of excited state molecular complexes called mixed-excimers which are exciplexes formed between pairs of molecules of similar but different species, such as molecules with a common aromatic core. Birks and Christophorou^{25,26} (1962) first observed a mixed-excimer fluorescence from systems like pyrene/l-methylpyrene. Several such systems have been reported to give this type of

fluorescence.^{27,28} The area of molecular complex formation involving aromatic systems has grown so much in depth and scope that no attempt will be made here to give a complete litany of them. Instead some broad classification will be given. This is necessary because, in addition to the excited state molecular complexes mentioned in the foregoing paragraphs, aromatic hydrocarbons and their derivatives are known to form stable ground state molecular complexes (both inter and intramolecularly). These ground state complexes may exhibit their unique absorption and emission bands. This situation has tended to create some confusion in the naming of molecular complexes. We will therefore make some classification of these complexes, not only with a view to presenting the acceptable descriptions for them, but also to identify the types that will be encountered in this work. Complex types, modes of formation and general characteristics are given in Table 1.1. In this work, we will be concerned with singlet state excimers and singlet state AD exciplexes - henceforth referred to as "exciplexes". Specifically, we will deal with naphthalene excimer and naphthalene-amine exciplex.

Thesis Objectives

Experimental and theoretical studies on intermolecular excimer and exciplex formation have shown that the most

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Complex Type	Mode of Formation	Characteristics
Excimer	A*+A + (AA)*	Broad, structureless emission; no corresponding absorption, and gener- ally solvent insensitive.
Mixed Excimer	A*+A' → (AA')*	Same as above.
Excited Dimer	(AA) [†] , (AA)*	Stable ground state; absorption spectra attributable to dimers, in- crease with concentration.
Photo-dimer	(AA) * → A ₂	A chemical entity formed from an excimer e.g., dianthracene ² 9,30.
AD Exciplex	A*+D ~ (A ⁻ D ⁺)*	Broad, structureless emission; no corresponding absorption;;solvent- sensitive (due to charge transfer character).
DA Exciplex	A*+D + (A ⁺ D ⁻)*	Same as in AD exciplex.
Electron-donor acceptor (EDA) complex	(A ⁻ D ⁺) + (A ⁻ D ⁺)*	Stable ground state; broad absorption band; often no emission in liquid solutions.
A is aromatic hydro electron donor (e.g tive of A).	carbon; A' is alkyl or ., aliphatic amine) or	allyl derivative of A; and D is either an an electron acceptor (e.g., cyano deriva-

Classification of Molecular Complexes of Aromatic Hydrocarbons. Table 1.1

probable conformation of these complexes in solutions of aromatic compounds is one in which the two components are in parallel-stacked face-to-face (sandwich) arrangement with a distance of 2.5-3.5 Å between them.³¹⁻³³ Indirect evidence for this conformation comes from the observance of excimer fluorescence from crystalline aromatic hydrocarbons in which the rings are oriented in a sandwich fashion. However, when the two interacting groups are bound in the same molecule, steric and entropy restrictions are introduced which strongly control the attainment of the favored sandwich conformation within the life time of the singlet excited state, which is on the order of 10^{-9} seconds. thus, the formation of intramolecular excimers and exciplexes is subject to certain geometrical requirements, the study of which has, not only thrown more light on the intrinsic nature of these complexes, but also has served as a reliable method of understanding configuration and conformation in chemical species in general, and in polymers in particular.

In vinyl polymers (for example) with pendant fluorescent aromatic groups, a molecular configuration, involving a three-carbon-atom separation between the aromatic moieties, has been found optimum $(n=3 \text{ rule})^{15}$ for intra-molecular excimer and exciplex formation. For a while, this rule seemed to have wide-spread validity in carbon-carbon chain composite and polymeric systems. However, exceptions soon began to surface, first for the case of intramolecular

U

exciplex formation. Ide et al³⁴ and Okada et al.³⁵ (1972), reported the occurrence, in polar solvents, of intramolecular cular exciplex emission in aromatic hydrocarbon-aromatic amine systems, in which the donor and acceptor groups are separated by one methylene group (n=1). This was attributed to increased complex stabilization via solvation, which seems to have overriden the geometric restrictions.

In 1973, Hayashi and Tazuke³⁶ searched unsuccessfully, for intra-molecular excimer emission in polyamides containing widely separated carbazole units in the backbone $(n \ge 6)$. To our knowledge, this was the only reported work for the case of heterochain polymers at the inception of this work. During the course of this work, Tazuke and Banba $(1976)^{37}$ reported the occurrence of intramolecular excimer formation in polyesters having pendant 1-naphthylmethyl groups separated by 16 carbon atoms and 2 oxygen atoms. Consequently, it seems obvious that the issue of geometric requirements for the formation of fluorescent intramolecular excimers and exciplexes remains an unsettled one. This work is intended to address this issue and other related excimerexciplex interactions along the following lines:

1. To synthesise and characterize a series of fluorescent polyamides with naphthyl groups in the backbone, with a view to investigate the possibility of intramolecular excimer formation between widely separated naphthyl groups (n>6). 2. To study the "polymer effect" on the reactivity of a molecular species (e.g., naphthalene) in intermolecular exciplex formation, involving the above polyamides, their monomer model compound and triethylamine.

3. To study the effects of solvent on intramolecular exciplex, formed in the monomer and related compounds, between the naphthyl group and the amino group separated by one methylene group (n=1).

4. To re-examine the controversial subject of exciplex interaction with small polar molecules, in order to shed more light on the mechanism involved in the interaction.

CHAPTER 2

THEORIES OF EXCITED STATE MOLECULAR COMPLEXES

EXCIMER STATE

Introduction

Experimentally, excimer formation has become a frequently occurring phenomenon in many aromatic systems in different environments. Its emission indicates a stable excited state and an unstable ground state; and its occurrence in aromatic crystals in which the rings are oriented in a sandwich fashion indirectly suggests a similar type of configuration for excimer in solution. These and other experimental findings formed the basis for theoretical investigations on the nature of the excimer state. Some of the fundamental questions are: what is the preferred steric configuration of the aromatic entities in the excimer? What type of forces hold them together? and what is the nature of the transient electronic structure?

Forster (1962)^{38,39} was the first to address these issues theoretically. He proposed that the excimer fluorescence occurred from the lowest excited singlet level of a l:l self complex; such level corresponds to the lowestenergy exciton component of the ¹La state of the aromatic hydrocarbon. Ferguson (1958)⁴⁰ suggested that the excimer
fluorescence could occur from a low energy charge resonance state of the dimer. Azumi and McGlynn $(1964)^{41}$ showed that neither the molecular exciton approach nor the charge resonance approach could lead to a satisfactory interpretation of excimer energies. Konijnenberg $(1963)^{42}$ introduced the configuration interaction model, in which the singlet excimer state is considered as a "mixed" state, produced by configuration interaction of charge-resonance and excitonresonance states. This approach was subsequently adopted by other workers.^{43,44} Thus, the general wave function, Ψ for the electronic states of the excimer entity can be written as:

 $\Psi \approx \Sigma a_{i} \Phi_{i} (A^{*}B) + \Sigma b_{i} \Phi_{i} (AB^{*}) + \Sigma C_{i} \Phi_{i} (A^{-}B^{+}) + \Sigma d_{i} \Phi_{i} (A^{+}B^{-})$ (2.1)

Exciton Resonance States Charge Resonance States Configuration Interaction States

In the following sections, we will describe in some detail, the three models for the excimer state: exciton resonance state, charge resonance state and configuration interaction state. This will be followed by a discussion on the extent to which each model or any combination of them, correctly accounts for the excimer binding energy.

Molecular Exciton Theory

The concept of the exciton was first introduced by J. Frenkel (1931)⁴⁵ to account for the dissipation into heat, of excitation energy in atomic crystals, following photon absorption. Frenkel realized that electronic excitation initially localized on a particular atom would, under the influence of the interatomic interactions, migrate to neighboring atoms. He called this migrating packet of electronic excitation energy, an "exciton". A. S. Davydov (1948)⁴⁶ used the molecular exciton concept to study the electronic states of naphthalene crystals. Subsequently, many problems in the area of molecular and solid state physics have been treated theoretically using the exciton theory.

A very simplified form⁴⁷ of this theory can be used to describe a self dimer consisting of an excited molecule and its ground state counterpart. Two degenerate time dependent wave functions ψ_1 and ψ_2 can be written:

$$\psi_1 = \phi_1^* \phi_2$$
$$\psi_2 = \phi_1 \phi_2^*$$

The stationary states of the dimer correspond to a linear combination of ψ_1 and ψ_2 . Such stationary states belong to different irreducible representation of the dimer point group. The first order energies can be found from the

determinant

$$H_{11} - E H_{12} = 0$$

 $H_{12} H_{22} - E$

where

$$H_{11} = H_{22} = \langle \phi_1^* \phi_2 | H | \phi_1^* \phi_2 \rangle$$
$$H_{12} = \langle \phi_1^* \phi_2 | H | \phi_1 \phi_2^* \rangle$$

(* denotes electronic excitation)

The roots of the determinant are

$$E' = H_{11} + H_{12}$$

 $E'' = H_{11} - H_{12}$

and the eigenfunctions are

$$\psi' = 2^{-1/2} (\phi_1 \phi_2 + \phi_1 \phi_2)$$
 (2.2)

$$\psi'' = 2^{-1/2} (\phi_1^* \phi_2 - \phi_1 \phi_2^*)$$
 (2.3)

 ψ^{*} and ψ^{*} are the stationary exciton states where the

excitation energy is delocalized over the two molecules forming the dimer. Evaluation of E' and E" yields

$$\mathbf{E'} = \mathbf{E}_{1}^{*} + \mathbf{E}_{2}^{*} \phi_{1}^{*} \phi_{2} | \mathbf{V}_{12} \phi_{1}^{*} \phi_{2}^{*} + \langle \phi_{1}^{*} \phi_{2} | \mathbf{V}_{12} | \phi_{1} \phi_{2}^{*} \rangle$$
(2.4)

$$E''=E_{1}+E_{2}^{*}+<\phi_{1}^{*}\phi_{2}|V_{12}|\phi_{1}^{*}\phi_{2}^{*}-<\phi_{1}^{*}\phi_{2}|V_{12}|\phi_{1}\phi_{2}^{*}^{*}$$
(2.5)

The last term in Equations (2.4) and (2.5) gives the "exciton splitting",

$$\Delta E = \langle \phi_1^* \phi_2 | V_{12} | \phi_1 \phi_2^* \rangle$$

.

 V_{12} can be expanded into a series of multipole-multipole interactions - that is dipole-dipole, dipole-quadrupole, quadrupole-quadrupole etc. For electric-dipole allowed transition, the most important term is the dipole-dipole interaction term. Using the point dipole-dipole approximation, V_{12} can be written as:

$$V_{12} = \frac{1}{R^3} [M_1 \cdot M_2 - \frac{3}{R^2} (M_1 \cdot R)M_2 \cdot R)]$$

where R is the intermolecular distance, and M_1 and M_2 are the transition moments of molecules 1 and 2. The exciton splitting term can also be written in terms of trignometric functions:

$$\Delta E = -|M_1|^2/R^3(2\cos\theta_1^2\cos\theta_2^2 - \cos\theta_1^y\cos\theta_2^y - \cos\theta_1^x\cos\theta_2^x) \quad (2.6)$$

 $\theta_1^{(x,y,z)}$ and $\theta_2^{(x,y,z)}$ are the angles which the transition moments, M_1 and M_2 respectively make with the x, y, z axes of the coordinate frame. The maximum exciton interaction will occur when the two transition moments are parallel to each other and at right angles to R ("perfect sandwich configuration) and the exciton splitting will be given by

$$\Delta E = -\frac{M^2}{R^3}$$
(2.7)

The validity of this expression in explaining the excimer binding energy will be examined later in the chapter.

Charge Transfer Theory

The formation of electron-donor-acceptor (EDA) molecular complexes by stable aromatic moleties has been known for years. One important phenomenological manifestation of such complexes is the appearance of intense absorption bands characteristic of the complex. Mulliken (1952)⁴⁸ developed the "charge transfer theory" to explain the electronic structure, and hence the absorption and emission characteristics of these complexes. His general theory of molecular complex formation is as follows: For a simple case of a 1:1 complex (D-A) formed by the weak interaction (dipoledipole, dipole-induced dipole dispersion interactions) of an electron donor (D) and an electron acceptor (A) molecules, the ground state wave function can be written as:

$$\Psi_0 = \Psi_0(D-A)$$

while the wave function of an ionic state (where an electron is donated to the acceptor) can be written as:

$$\Psi_1 = \Psi(D^+ - A^-)$$

A and D are assumed to be neutral, closed-shell molecules. The true ground state Ψ_N of the molecular complex is a mixed state of Ψ_1 and Ψ_0 , and the corresponding excited state is Ψ_E (charge transfer state)

$$\Psi_{\rm N} = a\Psi_0 + b\Psi_1 \tag{2.8}$$

$$\Psi_{\rm E} = a^{*}\Psi_{\rm O} - b^{*}\Psi_{\rm I}$$
 (2.9)

 $\Psi^{}_{\rm N}$ and $\Psi^{}_{\rm E}$ are orthogonal to each other, and on normalization yield

$$\langle \Psi_{N} | \Psi_{N} \rangle = \int \Psi_{N}^{2} d\tau = a^{2} + b^{2} + 2abS_{01} = 1$$
 (2.10)

$$\langle \Psi_{\rm N} | \Psi_{\rm F} \rangle = 0 \tag{2.11}$$

•_____

 ${\rm S}_{01}$ is the overlap integral between ${\Psi}_0$ and ${\Psi}_1 \colon$

$$S_{0l} = \int \Psi_0 \Psi_l d\tau$$

The eigenvalues corresponding to $\Psi^{}_{\rm N}$ and $\Psi^{}_{\rm E}$ are obtained by solving the secular equation

$$E_0 - E_N H_{01} - S_{01}E_N$$

 $H_{10} - S_{10}E_N E_1 - E_N$ (2.12)

where

$$E_{0} = \langle \Psi_{0} | H | \Psi_{0} \rangle; \qquad E_{1} = \langle \Psi_{1} | H | \Psi_{1} \rangle$$
$$H_{01} = \langle \Psi_{0} | H | \Psi_{1} \rangle; \qquad H_{10} = \langle \Psi_{1} | H | \Psi_{0} \rangle$$

For a weak complex, solution of equation (2.12) yields

$$E_{N} = E_{0} - \frac{(H_{01} - S_{01}E_{0})^{2}}{E_{1} - E_{0}}$$
(2.13)

$$E_{E} = E_{1} + \frac{(H_{01} - S_{01}E_{1})^{2}}{E_{1} - E_{0}}$$
(2.14)

If Ψ_0 and Ψ_1 have the same symmetry and spin multiplicity in the complex, then the smaller the energy difference $(E_1 - E_0)$ and the larger the value $(H_{01} - S_{01}E_0)^2$, the more stable the complex becomes. The potential energy curves corresponding to the ionic state, $(D^+ - A^-)$, the nonbonding state, D - A, the ground state and the charge transfer state of the complex are all shown in Figure 2.1, to illustrate the relations among E_0 , E_1 , E_N and E_E . R is the intermolecular distance between donor and acceptor; I_p is the ionization potential of the donor and E_A is the electron affinity of the acceptor.

An electronic transition from the ground state of the complex, E_N to its excited state, E_E , would then give rise to an absorption spectrum, with the transition energy given by:

$$hv_{CT} = E_E - E_N = E_1 - E_0 + \frac{(\alpha_0^2 + \alpha_1^2)}{(E_1 - E_0)}$$
 (2.15)

where $\alpha_0 = H_{01} - S_{01}E_0$ and $\alpha_1 = H_{01} - S_{01}E_1$; E_1 and E_0 can be approximated by,

$$E_{1} = E_{\infty} + I_{p} - E_{A} - C_{1}$$
$$E_{0} = E_{\infty} - C_{0}$$

where E_{∞} is energy at infinite separation of donor and acceptor molecules; C_1 is electrostatic energy and other weak interaction energies occurring between D^+ and A^- at



the equilibrium distance of the complex; and C_0 is the sum of several interaction energies between D and A, including electrostatic, dipole-dipole and van der Waals interaction. Then

$$E_1 - E_0 = I_p - E_A - (C_1 + C_0)$$

= $I_p - E_A - C$

so that equation (2.15) becomes

$$hv_{CT} = I_p - E_A - C + \frac{G}{I_p - E_A - C}$$
 (2.16)

where $G = (\alpha_0^2 + \alpha_1^2)$. For a weak complex, $I_p >> G$ or (E_A-C) consequently, its energy can be written:

$$hv_{CT} = I_p - E_A - C$$
 (2.17)

Equation (2.17) approximates the energy of a "pure" charge transfer (ionic) state, and its validity in accounting for the excimer binding energy will be seen shortly.

Excimer State - A "Pure" Exciton Resonance State?

The exciton resonance theory was first used by Forster 38 to explain excimer binding energy in aromatic hydrocarbons (e.g., naphthalene). He listed the following conditions

for excimer fluorescence to occur: (1) The lowest excited singlet state of the monomer should be the ${}^{1}L_{b}$ state, which has a small transition moment to the ground state, ${}^{1}A$. The relatively long life time 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. It is the transition from this lowest energy ${}^{1}L_{a}$ exciton component to the ground state to which Förster attributed the sandwich type excimer fluorescence, Figure 2.2.

The above conditions are not necessary for excimer fluorescence. Some molecules like 9-methylanthracene and pyrylene have ${}^{l}L_{a}$ as the lowest singlet excited state, and still show excimer fluorescence. Also condition (2) is not necessary as shown by Azumi and McGlynn, using the following arguments:

Using the exciton splitting, $\Delta E = M^2/R^3$, the calculated mutual separation R, which would yield the observed frequency difference between the ${}^{1}L_{a}$ level and the excimer fluores-cence in naphthalene is 1.8 Å, which is physically untenable.

Phenanthrene exhibits excimer fluorescence, however,



Förster's³⁶ Exciton Model of Excimer Formation in Aromatic Hydrocarbons. Figure 2.2.

according to Forster, the separation between ${}^{1}L_{a}$ and ${}^{1}L_{b}$ levels in phenanthrene is so large ($\sim 5000 \text{ cm}^{-1}$) that the exciton splitting of ${}^{1}L_{a}$ could not possibly produce a stable excimer state.

Thus, the excimer state cannot be described as a "pure" exciton resonance state.

Excimer State - A "Pure" Charge Resonance State?

The suggestion for the involvement of a charge resonance state in excimer binding energy was first made by Ferguson (1958)⁴⁰ for the case of pyrene crystals. This was later reiterated by Hochstrasser (1962)⁴⁹. And in 1963, Slifkin⁵⁰ extended this idea to excimers formed in solutions of a number of aromatic hydrocarbons including naphthalene.

The energy of the charge resonance state of an excimer can be expressed as:

$$hv_e = I_p - E_A - C \pm \Delta \qquad (2.19)$$

where Δ is the term resulting from the interaction of the two possible degenerate charge resonance states. With the assumption that $C \pm \Delta$ is constant, and using the values of $(I_p - E_A)$ obtained by Hedges and Matsen,⁵¹ Azumi and Mc-Glynn⁴¹ showed that $h\nu_e$ varied linearly with $I_p - E_A$. However, the $I_p - E_A - C$ values were found higher than the excimer fluorescence energies except at extremely low distance of separation. For example, in naphthalene: $I_p - E_A = 8.5 \text{ eV}, C \sim 3 \text{ eV}$ at 3 Å, giving that $I_p - E_A - C = 5.5 \text{ eV}$. But naphthalene excimer fluorescence energy is 3.13 eV. Consequently, the excimer state cannot be described as a "pure" charge resonance state.

Excimer State - a "Mixed" Exciton and Charge Resonance State

We have seen from the preceding sections that neither the exciton resonance state nor the charge resonance state adequately accounts for the excimer binding energy at reasonable distances of separation between the excimer components. It seems a logical option would be a "mixed" state produced by configurational interaction between the exciton resonance state and the charge resonance state; such option was suggested by Konijnenberg.⁴² McGlynn et al^{52} used this approach to study excimers formed by D_{2h} molecules such as naphthalene, anthracene and tyrene. What follows is an outline of their treatment, using naphthalene as an example. The relevant molecular orbitals (MOs) of naphthalene are sketched as shown on page 26. In the ground state electron configuration of molecule A, the next-to-highest and the highest filled MO's are represented as ϕ_0 and ϕ_1 , respectively, and the lowest and next-to-lowest energy vacant MO's as ϕ_2 and ϕ_3 ,



Molecule A Molecule B

respectively. The corresponding MO's of molecule B are θ_0 θ_1 , θ_2 , and θ_3 , respectively. The two lowest excited states of molecule A are ${}^{1}L_{a}$ and ${}^{1}L_{b}$. The ${}^{1}L_{a}$ excited state is produced by the excitation of an electron from the highest occupied orbital to the lowest vacant orbital, $\phi_1 + \phi_2$. The ${}^{1}L_{b}$ excited state is a resultant of the two zerothorder degenerate excitations: $\phi_1 + \phi_3$ and $\phi_0 + \phi_2$. The lowest energy excited states contributing to the excimer state are: charge resonance state and the two lowest exciton states, due to ${}^{1}L_{a}$ and ${}^{1}L_{b}$ excited states of the monomer. The wave functions of these excited states of the excimer can be written as: Molecular exciton states of ${}^{l}L_{a}$ origin:

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

where the bar denotes opposite spin.

Molecular exciton states of
$${}^{1}L_{b}$$
 origin:

$$\psi_{C} = |\phi_{1}\overline{\phi}_{1}\theta_{0}\overline{\theta}_{2}| - |\phi_{1}\overline{\phi}_{1}\overline{\theta}_{0}\theta_{2}| + |\phi_{1}\overline{\phi}_{1}\theta_{1}\overline{\theta}_{3}| - |\phi_{1}\overline{\phi}_{1}\overline{\theta}_{1}\theta_{3}|$$

$$\psi_{D} = |\theta_{1}\overline{\theta}_{1}\phi_{0}\overline{\phi}_{2}| - |\theta_{1}\overline{\theta}_{1}\overline{\phi}_{0}\phi_{2}| + |\theta_{1}\overline{\theta}_{1}\phi_{1}\overline{\phi}_{3}| - |\theta_{1}\overline{\theta}_{1}\overline{\phi}_{1}\phi_{3}|$$

Charge resonance states:

$$\psi_{\mathbf{E}} = |\phi_1 \overline{\theta}_2 \theta_1 \overline{\theta}_1| - |\overline{\phi}_1 \theta_2 \theta_1 \overline{\theta}_1|$$
$$\psi_{\mathbf{F}} = |\phi_1 \overline{\phi}_1 \phi_2 \overline{\theta}_1| - |\phi_1 \overline{\phi}_1 \overline{\phi}_2 \theta_1|$$

The above wave functions can be transformed into irreducible representations of the D_{2h} excimer point group by linear combinations of the corresponding functions: Molecular exciton (EXC) states

$$\Phi_{-}(^{1}L_{a}) = \psi_{A} - \psi_{B} : B_{3g}$$

$$\Phi_{+}(^{1}L_{a}) = \psi_{A} + \psi_{B} : B_{2u}$$

$$\Phi_{-}({}^{\perp}L_{b}) = \psi_{C} - \psi_{D} : B_{2g}$$
$$\Phi_{+}({}^{\perp}L_{b}) = \psi_{C} + \psi_{D} : B_{3u}$$

Charge resonance (CR) states:

$$\Phi_{(CR)} = \psi_{E} - \psi_{F} : B_{3g}$$

$$\Phi_+(CR) = \psi_E + \psi_F : B_{2u}$$

These results reveal that for a D_{2h} excimer, the ${}^{1}L_{a}$ exciton states transform identically with the charge-transfer states, while the ${}^{1}L_{b}$ exciton states transform differently from both ${}^{1}L_{a}$ exciton and charge-transfer states. There is nonvanishing configuration interaction between $|B_{2u}(exc)|$ and $|B_{2u}(CR)|$ and between $|B_{3g}(exc)|$ and $|B_{3g}(CR)|$. Consequently, the electronic states of the excimer are expressed by the superposition of the ${}^{1}L_{a}$ exciton (EXC) states and the charge resonance (CR) states:

$$\Psi(B_{3g}) = C_1 \Phi_{-}(^{1}L_a) + C_2 \Phi_{-}(CR)$$
 (2.20)

$$\Psi(B_{2u}) = C_3 \Phi_+ (^{1}L_a) + C_4 \Phi_+ (CR)$$
 (2.21)

where (C_1, C_3) and (C_2, C_4) are weighting factors for the molecular exciton states and charge resonance states,

respectively. Numeral calculations by McGlynn et al⁵² and other authors,^{43,44} unanimously show that the excimer fluorescence state (for many aromatic hydrocarbons) is ${}^{19}_{3g}$. For naphthalene excimer, the interplanar distance (R) at which calculated results give the observed excimer energy is 3.2 Å, which is reasonable, and compares well with the magnitude of intermolecular separation in molecular crystals exhibiting excimer emission. However, the above R value is dependent on the chosen effective nuclear charge, Z. In fact agreement with experiment is obtained only at Z > 3. This situation, thus casts some doubt on the real quantitative value of these semi-empirical techniques.

Exciplex State

The singlet exciplex state has been described as a charge transfer state, produced according to: 19,23

 $^{1}A^{*} + D + ^{1}(A^{-}D^{+}) \text{ or } A + D^{*} + ^{1}(A^{-}D^{+})$

where A is an electron acceptor and D is an electron donor. A molecular orbital diagram of the emissive exciplex state is given in Figure 2.3.⁵³ Indirect evidence in favor of the charge-transfer character of the exciplex comes from flash photolysis experiments in highly polar solvents, where transient absorption spectra due to the





radical anions have been observed.53

However, as the charge transfer complex state in most cases has an energy close to that of the lowest excited singlet states of the components, a more general description of the emitting exciplex state, which includes locally excited states, is given:

$$^{1}(A*D) \stackrel{Sad}{\leftrightarrow} (A^{-}D^{+}) \stackrel{S*}{\leftrightarrow} ^{1}(AD*)$$

The interactions of these locally excited states with the charge-transfer state depend upon the overlap integrals S_{ad} between the highest bonding orbitals and S_{ab}^* , between the lowest antibonding orbitals, respectively, leading to a stabilization of the emitting exciplex state. The wave function of the exciplex may be approximated as:

$$\Psi_{E} \approx \sum_{a_{i}} \Phi_{i}(A^{*}D) + \sum_{b_{i}} \Phi_{i}(AD^{*}) + \sum_{c_{i}} \Phi_{i}(A^{-}D^{+}) \qquad (2.22)$$

where $c_1 >> a_1 = b_1$

The energy of the "pure" charge-transfer exciplex state above the separated ground state components is given by:

$$E_{CT}^{o} = I_{p} - E_{A} - C$$
 (2.23)

where I_p is the ionization potential of the donor, E_A is the electron affinity of the acceptor and C is the coulomb attraction energy at equilibrium distance.

Exciplex Energy In Solution⁵⁴

The exciplex state is dipolar in character, so that in solution, its energy is expected to be lowered, due to solvation. The energy of the solvated exciplex can be determined as follows:

If the exciplex in solution is regarded as a point dipole, m, and if dipole-dipole interactions between it and the surrounding solvent molecules are considered, then the solvent dipoles will orient themselves relative to the exciplex; this will result in a decrease of the free energy of the total system. The orientation of the solvent dipoles will create an electric field, called the reaction field F, at the location of the exciplex. According to Onsanger simple continuum model, the reaction field on the solute dipole, with a dipole moment μ , situated at the center of a sphere of radius a, and surrounded by a homogeneous dielectric with dielectric constant, ε , is given by

$$F = \mu f_{c} \qquad (2.24)$$

where

$$f_{\varepsilon} = \frac{2}{a^3} \frac{\varepsilon - 1}{2\varepsilon + 1}$$
(2.25)

The energy of a dipole m, in an electric field F is given by

$$E_{m} = -\mu \cdot F \qquad (2.26)$$

The energy of polarization of the dielectric is

$$E_{pol} = \frac{1}{2} \mu \cdot F$$
 (2.27)

Thus, the free energy of solvation of the exciplex is given by

$$E_{s} = E_{m} + E_{pol} = -\frac{1}{2}\mu$$
 F (2.28)

Substituting for F, gives

$$E_{s} = -\frac{\mu^{2}}{a^{3}} \cdot \frac{\varepsilon - 1}{2\varepsilon + 1}$$
(2.29)

If we represent the Hamiltonian of the exciplex in the gas phase by H°, and the eigenfunctions by Ψ° , then in solution, the reaction field caused by solvation will act as a perturbation, given by the Hamiltonian, H¹

$$H^{1} = -\mu_{op} \cdot F$$
 (2.30)

(where $\mu_{\mbox{\scriptsize op}}$ is dipole moment operator) so that the total Hamiltonian H, is given by

$$H = H^{\circ} + H^{1}$$
 (2.31)

The wavefunctions of the perturbed states are given by

$$\Psi = \sum_{i} C_{i} \Psi_{i}^{\circ} \qquad (2.32)$$

$$\mu = \langle \Psi \mu_{op} \Psi \rangle \tag{2.34}$$

The solution of Ψ is a self-consistent field problem. In addition to the above electronic perturbation, the equilibrium values of λ_j° , of the geometric parameters, λ_j of a non-rigid exciplex, will depend on the polarity of the solvent (ε) and also on the condition

$$\left(\frac{\partial E_{a}(\lambda_{j})}{\partial \lambda_{j}}\right)_{\varepsilon \lambda_{1}^{\circ}} = 0$$

for all j; where E_a is the free energy of solvation of the exciplex.

$$E_a = E + E_{pol}$$
(2.35)

$$E = \langle \psi(\lambda_{j}) | H^{\circ}| (\lambda_{j}) + H^{1}(\lambda_{j}) | \psi| (\lambda_{j}) \rangle$$
 (2.36)

and

$$E_{pol} = \frac{1}{2} \mu(\lambda_j) F(\lambda_j)$$
 (2.37)

If we consider an exciplex, in which only one locally excited state (AD)* interacts with the CT state $(A^{-}D^{+})$,

the wave function Ψ can be represented by

$$\Psi = C_{1} \Psi (A^{-}D^{+}) + C_{2} \Psi (AD) *$$
 (2.38)

The matrix element $\langle \psi(A^{-}D^{+})|\mu_{op}|\psi(AD)^{*}$ vanishes, if intermolecular overlap is neglected. Also, if the dipole moment in the state (AD)* is zero, the final dipole moment, μ is given by

$$\mu = C_1^2 \langle \psi(A^- D^+) | \mu_{op} | \psi(A^- D^+) \rangle = C_1^2 \mu_o$$
(2.39)

where μ_{0} is the dipole moment of $(A^{-}D^{+}),$ and under normalization condition

$$C_1^2 + C_2^2 = 1 \tag{2.40}$$

The Hamiltonian matrix elements of the exciplex in the gas phase are denoted by

$$\langle \psi(A^{-}D^{+})|H^{\circ}|\psi(A^{-}D^{+})\rangle = E_{c}$$
 (2.41)

$$<\psi(AD)*|H^{\circ}|\psi(AD)*> = E_{a}$$
 (2.42)

$$\langle \psi(A^{-}D^{+})|H^{\circ}|\psi(AD)^{*}\rangle = \alpha$$
 (2.43)

Using Equations (2.24), (2.30) and (2.39), the matrix element of the exciplex in solution is given by

$$\langle \psi(A^{-}D^{+})|H^{1}|\psi(A^{-}D^{+})\rangle = -C_{1}^{2}\mu_{0}f_{\varepsilon}$$
 (2.44)

This approximates the influence of the solvent in terms of changing the energy difference between the zero-order states $(A^{-}D^{+})$ and (AD^{*}) . Thus, applying the variation principle, and substituting equations (2.41) - (2.44), leads to the secular equations

$$C_1(E_c - C_{1\alpha}^2 f_{\epsilon} - E) + C_{2\alpha} = 0$$
 (2.45)

$$C_1 \alpha + C_2 (E_0 - E) = 0$$
 (2.46)

which can be combined to give

$$(E_{c} - E - \frac{\alpha^{2}}{E_{e} - E})(1 + \frac{\alpha^{2}}{(E_{e} - E)^{2}}) = \mu_{o}^{2}f_{E}$$
 (2.47)

where E is the energy of the resulting exciplex states. When E is calculated, C_1^2 can be obtained from Equations (2.40), (2.45) and (2.46)

$$C_{1}^{2} = \{1 + \frac{\alpha^{2}}{(E_{p} - E)^{2}}\}$$
 (2.48)

From Equations (2.24), (2.28) and (2.44) the polarization energy, E_{pol} stored in the solvent can be obtained,

$$E_{pol} = \frac{1}{2} C_{1}^{4} \mu_{0}^{2} f_{\varepsilon}$$
 (2.49)

The energy of the Frank-Condon (FC) ground state, E_g^{FC} to which the exciplex transition occurs can be written

$$E_{g}^{FC} = E_{g}^{o}(1 - \frac{f_{1}}{f})E_{pol}$$
 (2.50)

where

$$f^{1} = \frac{1}{2}a^{3}f_{n} = \frac{n^{2}-1}{2n^{2}+1}, f = \frac{1}{2}a^{3}f_{\varepsilon} = \frac{\varepsilon-1}{2\varepsilon+1}$$
 (2.51)

(n = refractive index of the solvent), and E_g^o is the gas phase energy of the ground state.

The frequency of the exciplex emission is given by

$$hv_E = E_a - E_g^{FC}$$
(2.52)

Thus, using equations (2.24), (2.35), (2.36) and (2.50-2.52), and assuming that the excited dipole moment, μ_{e} , of the emitting exciplex is independent of the solvent, then the exciplex emission frequency becomes

$$hv_{\rm E} = hv_{\rm E}(0) - \frac{2\mu^2}{a^3} (f - \frac{1}{2}f^1)$$
 (2.53)

Exciplex energies calculated from Equation (2.53), may deviate significantly from experimentally observed values, because some of the approximations involved in its derivation are rather too simplified, if not far from reality. For example, polar molecules are not expected to form a spherical dome around the exciplex. Their structure may be such that neighboring dipoles can approach the central dipole (exciplex) to within distances smaller than 2a. It is hard to estimate the error due to any difference in the structure of actual molecules and Onsanger's model. Any such departure, will however, make the true reaction field, F, greater than that calculated from Onsanger's model.

Also, at short distances, it seems untenable to consider the environment of the central dipole as a continuum, since the amount of polarizable matter contained in a continuum will be greater (by say a factor α) than the amount contained in the discontinuous environment. Consequently, the reaction field calculated on the basis of a continuous environment of the central dipole will be too large by approximately the factor α .

Finally, the neglect of specific exciplex-solvent interaction (which can occur in polar media) is surely not a sound assumption; and it will be the subject of a separate and detailed investigation in Chapter 7 of this thesis.

CHAPTER 3

SYMTHESIS OF POLYAMIDES AND THEIR MONOMER ANALOGS

Introduction

Most of the studies to date on intramolecular excimer formation in polymers have involved olefinic type polmers, 15,16,57 such as polystyrene, polyvinylnaphthalene, polyacenaphthalene, etc., which either, are commercially available or can be easily made from readily available monomers. On the other hand, fluorescent heterochain polymers, apart from biopolymers, are not commonly available; the same is true of their monomers. This seems to account for the little attention, heterochain polymers have received in the literature 36,37 to date, in studies of geometric requirements for excimer formation.

This is in spite of the fact that heterochain (polycondensation) polymers have a number of structural advantages over the olefinic polymers in studying molecular interactions in relation to polymer structure (as in excimer formation). These are: skeletal flexibility; ease of variation of distance of separation between chainincorporated fluorophores, and a high degree of accuracy in distribution of groups in the chain. In vinyl-type polymers, uncertainty in polymer structure, arises mostly from the existence of a strong probability for head-tohead and tail-to-tail addition of the monomer in the

propagation stage.

It seems therefore rational to take advantage of these structural features offered by heterochain (polycondensation) polymers, notwithstanding any concomittant synthesis. In this chapter, we will discuss the synthesis of: diamine monomers - 2,6-bis(methyl amino) naphthalene and 2,6-bis(N methyl, methyl amino)naphthalene; and the synthesis of polyamides derived from them by interfacial colycondensation, with a series of diacid chlorides. These polyamides have the following structural features - a built-in fluorescent moiety (naphthalene) in the backbone; and with the said fluorescent group separated from the amide linkage by a methylene group. This type of polyamide structure offers a number of additional advantages in fluorescence studies: it allows for a direct monitoring of "micro" and macro-brownian motions of the polymer chain by fluorescence quenching and depolarization tion; it also prevents any significant ground-state electronic perturbation of the fluorescent aromatic group by the amide group. We will also discuss the synthesis of a few more compounds: 2,6-bis(N-methyl,N-acetyl, methyl amino) naphthalene - mcdel compound for the above polyamides; 2,6-bis(N-dimethyl, methyl amino)naphthalene, synthesized to probe solvent-induced intramolecular exciplex emission; and finally 2,6-bis(bromomethyl)naphthalene - the starting material for the preparation of the diamines.

2,6-Bis(bromomethyl)naphthalene (3)



2,6-Bis(bromomethyl)naphthalene (3) was obtained by refluxing a mixture of 2,6-dimethylnaphthalene (1), Nbromosuccinimide (2) and benzoyl peroxide, in benzene. 58 Under heat, and in the presence of a free radical initiator, bromination occurs predominantly in the side chain. The resulting product, on crystallization with a 1:3 mixture of chloroform and tetrahydrofuran gave rod-like crystals (slightly colored yellow). Multiple recrystallization was therefore undertaken to get colorless crystals; yield 31.4%. This low yield could result from the formation of a number of competitive products; for example, the di-, and tribromo derivatives, and even some ring bromination products. The melting point of the product (182-184°) agrees with that reported in the literature,

 $(182-184^{\circ})^{59}$.

The product was used in the synthesis of 2,6-bis(methylamino)naphthalene (6) and its N-methyl derivatives (8 and 10).

2,6-Bis(methylamino)naphthalene (6)

This compound was prepared according to the reaction scheme:



The first step in the reaction is a straight forward ammonolysis of the bromide (3). However, this method of synthesis of amines has a serious disadvantage of yielding a mixture of primary, secondary, tertiary and quarternary amines. The formation of the last three products can be reduced by using a large excess of ammonia, preferably pure liquid ammonia. However, attempts to use pure liquid ammonia in sealed tubes at room temperature, led to explosions. So, ethanolic solution of ammonia (large excess) was used. The reaction mixture was refluxed at 30° with a cold finger attached to the reaction flask. The resulting amine salt was treated with sodium hydroxide solution to give the free amine. Recrystallization with a 1:3 mixture of methylene chloride and cyclohexane gave a white fluffy powder; yield, 57.4%; mp 125-130°.

Structural identification of product was done by nmr and mass spectra. The mass spectrum showed a base peak at M/e 186 (parent) and another intense peak at M/e 156 $(P-\dot{C}H_2NH_2)$. Nmr spectra (Figure 3.1b) indicate the presence of the expected groups: $-NH_2(\delta 1.58)$, $>CH_2(\delta 3.95)$ and naphthalene ($\delta 7.27-7.77$). The $-NH_2$ protons give a sharp singlet because they are decoupled from the nitrogen and from the adjacent $>CH_2$ protons (due to fast exchange). For the same reason the $>CH_2$ peak is a singlet. This behavior is typical of most aliphatic amines.

Product (6) was used in interfacial polycondensation with glutaroyl, suberoyl and sebacoyl chlorides to give polyamides, which were intended for use in fluorescence studies. However, because they proved highly insoluble, their N-methyl derivatives were prepared and used instead. Further use of product (6) was in the study of intramolecular exciplex formation (Chapter 6).



Figure 3.1. NMR spectra: a) 2,6-Dimethyl naphthalene (1), (b) 2,6-Bis(methylamino)naphthalene (6), (c)2,6-Bis(N-methyl, methylamino) naphthalene (8), (d) 2,6-Bis(N-dimethyl, methylamino)naphthalene (10).





Compound (8) was prepared by treating 2,6-bromomethylnaphthalene with a large excess of methylamine, dissolved in ethanol. The reaction mixture was refluxed at 45°, and trapped with a cold finger. The resulting amine salt (white) was dissolved in dilute hydrochloric acid solution; on treating this solution with sodium hydroxide, it was discovered that precipitation occurred in two distinct stages - first a milky precipitate (probably tertiary and/or quarternary amines), then followed by a silvery-white, flake-like precipitate (identified as the product). Thus, recovery of the free amine was accomplished by fractional precipitation from an aqueous solution of the amine salt. Yield, 86%; mp 52-60°. The molecular formula $(C_{14}H_{18}N_2)$ of compound (8) was confirmed by elemental analysis. Its structure was elucidated from nmr and mass spectra. The latter showed peaks at: M/e 214 (parent, 64%), M/e 42 (base, $\dot{C}H_2-N=CH_2$) and M/e 44 ($\dot{C}H_2NH$, intense). Nmr spectra (Figure 3.1c) CH_2

show the presence of the expected groups: $>NH(\delta 1.40)$, $CH_2(\delta 3.80)$, $>NCH_3(\delta 2.43)$, and naphthalene ($\delta 7.22-7.72$). The absorptions of >NH and $>CH_2$ protons have shifted slightly upfield (cf. Figure 3.1b), due to electron donating effect of the methyl group on nitrogen. The labile nature of >NH proton is shown by effect of deuteration (Figure 3.2b); also its intensity is considerably enhanced by water (Figure 3.2a - spectrum of a partially dried product), further confirming the active nature of this hydrogen.

Product (8) was used in interfacial polycondensation with a series of diacid chlorides to give N-methylated polyamides (14), that were soluble. Also, the product was used extensively in the study of intramolecular exciplex formation (Chapter 6).



Figure 3.2. NMR spectra: a) 2,6-Bis(N-methyl, methyl amino)naphthalene, b) (a) - deuterated, c) 2,6-Bis(N-methyl, N-acetyl, methylamino)naphthalene.


2,6-Bis(N-dimethyl, methyl amino)naphthalene (10)

The synthesis of this compound was effected by reacting 2,6-bis(bromomethyl)naphthalene (3) with dimethylamine (liquid) under the same reflux conditions used for the monomethyl derivative (8); product recovery was similarly carried out. Yield, 85.3%; mp 100-103°.

The molecular formula $(C_{16}H_{22}N_2)$ of compound (10) was confirmed by elemental analysis. The mass spectrum showed a number of expected peaks: M/e 58 (base, $\dot{C}H_2N(CH_3)_2$), M/e 242 (parent, 41%) and M/e 198 (P- $\dot{N}(CH_3)_2$, 50%). Nmr spectra (Figure 3.1d) confirm the presence of: $>CH_2(\delta_{3.50})$, - $N(CH_3)_2(\delta_{2.25})$ and naphthalene ($\delta_{7.23}$ -7.72).

Product (10) was used in the study of intra-molecular exciplex formation (Chapter 6) and in the investigation of exciplex interaction with small polar molecules (Chapter 7).



2,6-Bis(N-methyl,N-acetyl, methylamino)naphthalene (11)

The polyamide model compound (11) was made by acylation of 2,6-bis(N-methyl, methylamino)naphthalene (8) with acetyl chloride in chloroform. An excess amount of the diamine was used to remove hydrochloric acid (condensation by-product). Recrystallization with a mixture of ether and chloroform gave colorless plate-like crystals; yield, 49%, mp 202-204°.

The molecular formula $(C_{18}H_{22}N_2O_2)$ of compound (11) was confirmed by elemental analysis. The mass spectrum gave the following expected peaks: M/e 298 (parent, 18%), M/e 225 (base, P-HNCOCH₃), M/e 255 (P-COCH₃, 48%, and M/e CH₃

226 (P-NCOCH₃, 51%). Nmr spectra (Figure 3.2c) reveal the CH₃

expected groups: $>CH_2(\delta 4.60, \delta 4.67)$, $>NCH_3(\delta 2.90, \delta 2.95)$, -COCH₃($\delta 2.17$) and naphthalene ($\delta 7.22-7.75$). The absorptions of $>CH_2$ and $>NCH_3$ protons appear as two-component peaks as a result of non-equivalence caused by hindered rotation around the amide group.

Product (11) was used as the model compound for polyamides (14) in the following studies: intramolecular excimer formation (Chapter 4) and "polymer effect" in molecular interactions (Chapter 5).

Polyamides by Interfacial Polycondensation

The well-known Schnotten-Bauman⁶⁰ reaction for acvlating amines and alcohols is the basis for interfacial polycondensation - an extremely versatile method, employed here for the synthesis of polyamides of 2,6-bis(methylamino)naphthalene (6) and 2,6-bis(N-methyl, methylamino) naphthalene (8). The reaction is believed to take place at the interface between a solution of a diacid chloride in a water-immiscible organic solvent and a water solution of, for example, a diamine, containing an acid acceptor. It is a fast, low-temperature reaction, usually complete in 1-5 minutes. The reaction is also insensitive to reactant equivalence and tolerant to the presence of many impurities in the reactants that have only dilution effect, such as water, or salt in the diamine or an inert liquid in the acid chloride. However, one serious disadvantage of this process is the hydrolysis of the acid chloride - the shorter-chain aliphatic diacid chlorides being most affected. This could lead to low or no yield of high molecular

weight polycondensation products.

The procedure for mixing the reactants is to dissolve both the diamine and an acid acceptor in water, and with this aqueous solution vigorously stirred, the diacid solution is quickly added. However, adoption of this procedure in our case, led to precipitation of the diamine from the aqueous solution prior to the addition of the acid chloride. Consequently, a separate aqueous solution of an acid acceptor-sodium hydroxide had to be made, and was added simultaneously with the acid chloride. Also, in all of the polyamide synthesis, excess diacid chloride was used for two reasons: to compensate for losses of the acid chloride due to hydrolysis, and to ensure total consumption of the diamine, which could otherwise contaminate the polymer, and would absorb and emit at the same wavelength region. Consequently, the terminal groups in these polyamides are most likely the respective acid chloride groups, or ethoxy groups resulting from reaction with ethanol in the solvent-chloroform (a commercial sample with 0.75% ethanol as a preservative.

Polyamides of 2,6-Bis(methylamino)naphthalene (13)



An aqueous solution of diamine (6) and a chloroform solution of the diacid chloride: glutaroyl chloride (x=3), suberoyl chloride (x=6) or sebacoyl chloride (x=8) were allowed to react as described in the preceding section. The resulting polyamides (white solids) were recovered by filtration. Products were dialyzed for 24 hours to remove small molecule impurities, and then vacuum-dried at 62°; the final products were creamy white, with yields: P3-13 (40%), P6-13 (70\%) and P8-13 (63\%). Their melting temperatures were above 300°.

The polymers could not be dissolved in any solvent;

not even in strongly acid solvents (for example sulfuric acid and trifluoroacetic) nor in phenols (like m-cresol). These solvents are generally used to dissolve polyamides. Consequently, some structural modification had to be made to solubilize the polyamides. Polyamides are generally, difficultly soluble, owing to their partial crystalline nature. This crystallinity arises from intermolecular hydrogen-bonding through the amide linkages. Shashoua and Eareckson⁶¹ found that polyterephthalamides from primary aliphatic diamines were soluble only in the strongly acidic solvents; however, on replacing the amide hydrogen by alkyl groups, several of the polymers became soluble in chloroform, acetone, aqueous alcohol, 80%, and dimethylformamide. They also found that N-alkylation led to a substantial lowering of the polymer melt temperature. All this, is as a consequence of the loss of interchain hydrogen bonding, on N-alkylation. The result - non-crystalline (amorphous) polyamides, with remarkably good solubility properties. This offered us a good prospect, not only from the stand point of getting these polymers into solution in the first place, but also, of having some flexibility in using solvents that are suitable for fluorescence studies. Consequently, 2,6-bis(N-methyl, methylamino)naphthalene (8) was synthesized for making the N-methylated derivatives of the insoluble polyamide series (13).

Polyamides of 2,5-bis(N-methyl, methylamino)naphthalene (14)



With the exception of P8-14 synthesis (in which carbon tetrachloride was used in place of chloroform) the polycondensation reactions were performed in a chloroform/ water mixture. Use of carbon tetrachloride as a solvent, led to precipitation of the polymer during the course of the reaction. The solid product was colored dirty brown. This was dissolved in chloroform, and treatment with methanol, did not precipitate the polymer. In the cases where the reaction was performed in chloroform/water mixture, the polymer went into solution in chloroform layer (generally colored brown). Reduction of the volume of chloroform layer, followed by addition of methyl alcohol caused precipitation of P2-14 and P4-14 out of solution but not P3-14 and P6-14. Cyclohexane and n-hexane were tried as precipitants; this led to brown rubbery solids, instead. Consequently, product purification in P6-14 and P8-14 synthesis had to be accomplished by repeatedly dispersing the solid polymer into fine particles in methanol to dissolve as much of the impurities as possible - this method yielded creamy white products. However, this approach failed to rid P3-14 product of its dirty brown color; it was therefore not used in the photophysical studies.

The following yields were obtained: P2-14 (44%), P4-14 (27%), P6-14 (2.6%) and P8-14 (30%). These yields are comparatively lower than those obtained with the primary diamine (6). This is not surprising, since the secondary diamine (8) is expected to be less reactive than the primary diamine because of steric hinderance. The low yields could also result from the hydrolysis of the diacid chlorides; no products were obtained with malonyl and oxaloyl chlorides, probably because they are highly susceptible to hydrolysis.

The melt temperatures of the polymers are: P2-14 (115-120°), P4-14 (193-195°), P6-14 (115-126°) and P8-14 (123-125°). There is thus a substantial lowering in melting temperature as a result of N-methylation. These polyamides are soluble in: chloroform (extremely), ethanol/chloroform (3:1) mixture, and methylene chloride (with warming). In the presence of small amounts of a non-solvent (for example cyclohexane) the polyamides become plastic, and

gradually turn into rubbery materials as the amount of non-solvent is increased. Thus, while thermodynamically "good" solvents dissolve the polymers with ease, non-solvents act as plasticizers or flexibilizers. The implication of all this, is that the forces of cohesion between the polymer molecules in the N-methylated polyamides are easily diminished by solvent molecules, following the destruction of their hydrogen bonding capability. We thus have made a soluble amorphous polyamide series, with linear and flexible chains - these characteristics will prove useful in studying inter- and intra-molecular interactions in solution.

<u>Structural Analysis of Polyamides of 2,6-bis(N-methyl,</u> methylamino)Naphthalene (14)

A somewhat limited but adequate identification of these polyamides was performed, as low yields were obtained in most cases. Their chemical compositions and structures were established by elemental analysis and nuclear magnetic resonance spectra, respectively; while an estimate of the magnitude of their molecular weight was obtained by viscometric measurements carried out with one member of the series.

Results of elemental analysis on P2-14, P4-14 and P8-14 for carbon and hydrogen, show excellent agreement between the calculated and the found, only for hydrogen;

while sizeable deviations occur in carbon content: 3.6% in P2-14 and P4-14, and 1.5% in P8-14. The calculated elemental composition was based on the repeating unit of each polymer: which does not take into account the end groups. However, it is unlikely that exclusion of two small-molecular units per polymer molecule, would introduce any significant error when we are dealing with molecular weights on the order of 20,000 (see next section). And, if the discrepancy in carbon content is due to organic impurities, one would expect the hydrogen content to be similarly affected. But this was not the case, which leaves one to speculate that the experimentally-determined carbon contents could be in error. A repeat of elemental analysis was not undertaken because sufficient structural evidence was obtained from nmr spectra (Figure 3.3) of dilute solutions of the polymers in CDCl₂, with TMS as reference.

The NMR peaks are broadened; this is generally the case in solutions of high molecular weight polymers. The line broadening arises from direct dipole-dipole interactions, as a result of restricted molecular motion in polymeric systems. The presence of the diamine (8)-monomer unit in the polymer structure is confirmed by the absence of \geq NH group (δ 1.4) and the presence of the following groups: \geq CH₂ (attached to ring) (δ ~4.65), \geq NCH₃ (δ ~2.90) and naphthalene (δ 7.22-7.74). The respective diacid chloride units



Figure 3.3. NMR spectra: a) 2,6-Bis(N-methyl, N-acetyl, methylamino)naphthalene, b) P2-14, c) P4-14, d) P6-14, e) P8-14.

in the polymer chain, give rise to methylene proton absorptions at higher fields, identified as follows: terminal >CH₂ protons (next to carbonyl groups) absorb at lower fields ($\delta \sim 2.35$) than the penultimate >CH₂ protons: $\delta 1.78$ (P4-14), $\delta 1.67$ (P6-14) and $\delta 1.70$ (P8-14), while the internal >CH₂ protons in P6-14 and P8-14 occur at much higher field, $\delta \sim 1.4$.

Ratios of peak areas are given below, starting from low to high field absorptions, with expected values in brackets:

P2-14, 1.4:1:1.4:0.8 (1.5:1:1.5:1)
P4-14, 1.2:1:1.5:0.9:1(1.5:1:1.5:1:1)
P6-14, 1.5:1:1.6:0.8:1.8(1.5:1:1.5:1:2)
P8-14, 1.2:1:1:1.3:1.3:3.4(1.5:1:1.5:1:3)

Within the limits of experimental error, there is agreement between the experimentally determined peak ratios and the expected, thus confirming the chain structures established by chemical shifts.

The spectra of P2-14 show a two-component peak at $\delta 2.77$ and $\delta 2.95$, assigned to $>NCH_3$ protons (Figure 3.3b). A similar peak is seen in the spectra of the polymer model compound (Figure 3.3a). The two-component nature of both peaks is believed to arise from the non-equivalence created by restricted rotation about the amide group.

Molecular Weight Determination

A relatively quick and reliable method of determining the molecular weight of a polymer involves the use of the Mark-Houwink expression:

$$[\eta] = KM^a$$

where [n] is the intrinsic viscosity, M is the molecular weight, and K and a are constants for the polymer-solvent system at a particular temperature. Values for K and a for many systems are available in the Polymer Handbook.⁶²

The intrinsic viscosity is obtained by means of expressions derived by Huggins and Kraemer, which give relative viscosities as a function of concentration:

Huggins equation

$$n_{n} - 1/C = [n] + K_{1} [n]^{2}C \qquad (3.1)$$

Kraemer equation

$$\ln n_{r} / C = [n] - K_{2} [n]^{2} C \qquad (3.2)$$

where n_r is the relative viscosity at concentration C, and k_1 and k_2 are constants. A plot of n_r -1/C and/or lnn_r/C against C would yield [n] as the intercept.

Relative viscosity measurements were done with polymer

P2-14 using a Cannon-Ubbelohde viscometer. The temperature of the viscometer and its contents was kept constant to within $\sim 0.02^{\circ}$ C by means of a thermostated water bath. Efflux time at any chosen concentration was taken about five times to get at least three readings that agreed to within 0.05 sec. A Kraemer plot (Figure 3.4) gave a value of 0.55 for [n], from which a molecular weight of $\sim 20,000$ was estimated for P2-14.



Figure 3.4. Determination of Intrinsic Viscosity of Polymer P2-14.

CHAPTER 4

INTRAMOLECULAR EXCIMER FORMATION IN POLYAMIDES HAVING NAPHTHYL GROUPS IN THE BACKBONE

Introduction

Hirayama's work on diphenyl and triphenyl alkanes¹⁵ (prototypes of vinyl polymers) showed that only 1,3-diphenyl propane and 1,3,5-triphenyl pentane exhibited intramolecular excimer fluorescence. This led him to propose what is today known as Hirayama's "n=3 rule", which states that intramolecular excimer formation will occur only when the aromatic chromophores are separated by a chain of three carbon atoms. This geometric restriction arises in that the optimum condition for excimeric interaction is one in which the components are in a symmetrical parallel-sandwich configuration. This configuration is attainable for n=3; however, for n=1 and n=2, it is impossible, without deforming the tetrahedral bond angle of the alkane chain; while for n>3, conformational instability due to steric interaction makes such a sandwich configuration difficult to reach.

An enormous amount of work was undertaken in the early days to verify the "n=3 rule", and results from these studies tended to confirm the rule: Yanari, et al. 18

(1963) made the first observation of intramolecular excimer fluorescence in isotactic polystyrene. Vala, et al.¹⁶ (1965) reported its occurrence in polystyrene (atactic and isotactic) and in atactic poly(1-vinylnaphthalene). Klöpffer⁶³ (1969) observed a weak intramolecular excimer fluorescence in 1,3-biscarbazolylpropane. Chandross and Dempster⁶⁴ (1970) studied α,ω -dinaphthyl alkanes and found that only 1,3-dinaphthylpropane showed intramolecular excimer fluorescence. Johnson and Offen⁶⁵ (1971) reported the case of poly(N-vinylcarbazole); and Fox, et al.⁶⁶ (1972) observed intramolecular excimer formation in poly-(2-vinylnaphthalene).

One must point out, however, that all of the above composite and polymeric systems have one thing in common: a three-carbon chain separating the two interacting chromophores. The question then arises: will the 'n=3 rule' apply with the same strictness in heterochain systems? The first clue to the answer to this question was perhaps the work of Longworth⁶⁷ (1966), who reported the occurrence of intramolecular excimer formation in poly(L-phenylalanine), poly(1-benzyl-L-histidine) and poly(β -benzyl-L-aspartic acid). In the first two polypeptides, the phenyl groups are separated by 5 carbon atoms and 1 nitrogen atom; while in the last compound, 6 carbon atoms and 1 nitrogen atom separate the interacting groups. Ten years later, Tazuke and Banba³⁷ observed weak intramolecular excimer fluorescence in some polyester series and their dimers, in which

pendant naphthyl groups are separated by as many as 16 carbon atoms and 2 oxygen atoms. And quite recently, DeSchryver, et al.⁶⁸ (1977), observed intramolecular excimer formation in α, ω -dianthryl esters, in which the chromophores are separated by upwards of 7 carbon atoms and 2 oxygen atoms. The conclusion to all these observations is that heterochain systems do not seem to comply strictly with the "n=3 rule" most probably, as a consequence of the flexibility of the chain containing hetero atoms. And one obvious implication of the behavior of the above heterochain systems is that it emphasizes the importance of the chemical constitution of the chain in influencing intramolecular excimer interaction.

Exceptions to the n=3 rule for carbon chain systems were reported. Zachariasse and Kühnle⁶⁹ (1976) showed that intramolecular excimer fluorescence occurs in α,ω di-(1-pyrenyl)alkane Py(CH₂)_nPy for n=2-6, 8-12 and 22. One wonders why it took so long to discover such serious exceptions to this rule. One obvious reason is the narrow choice of fluorescent moieties. The early workers used virtually only <u>phenyl</u>, <u>naphthyl</u> and <u>carbazolyl</u>-containing systems which were readily available as vinyl polymers, and simple bichromophoric alkanes. It turned out that the above three aromatic groups have the following shortcomings, compared to pyrene moeity:

i) Shorter monomer fluorescence lifetime (for example,

toluene-39 nsec and β -methylnaphthalene-59 nsec); while pyrene has a lifetime of 250 nsec.

ii) Smaller intermolecular excimer stabilization energy $(-\Delta H)$, which is on the order of 5 kcals mole⁻¹ compared to 10 kcals mole⁻¹ for the pyrene excimer.

The above two factors are surely essential in intramolecular excimer formation:

a long-lived excited singlet state would lead to increased probability of encounter between chromophores, widely-separated in a chain.

and when such an encounter occurs, the binding energy of the resulting excimer will depend on the extent of orbital overlap, which in turn depends on the electronic and geometric structure of the aromatic moiety.

The crucial role of these two factors in determining the occurrence of intramolecular excimer fluorescence, is clearly demonstrated in the case of $Py(CH_2)_n Py$.

In the foregoing review, three factors are seen to exercise significant control on intramolecular excimer formation, namely:

Length of chain; Chemical constitution of chain; and Electronic and geometric structure of the aromatic moiety. From the results of the work of Zachariasse and Kühnle, cited earlier, it would appear that the third factor above - the nature of the fluorescent group, is the predominant factor.

The work to be described in this chapter will focus on the effect of the intervening chain (its length and chemical constitution) on the probability of forming excimers and the importance of the "n=3 rule" for a given series of bichromophoric or polychromophoric systems. This work will also add to the increasing evidence, obtained from studies of intramolecular excimer formation in homopolymers and copolymers alike, that chain coiling in polymers can produce geometries favorable to excimer formation between non-adjacent chromophores. Currently, the picture is not clear: for example, while it is justifiable to attribute intramolecular excimer formation in poly(acenaphthalene)⁷⁰ in dilute solution to interactions between chromophores on adjacent turns of the polymer coil, because face-to-face interactions between adjacent rings are unlikely, such proposition in the case of poly(N-vinyl carbazole)⁶⁵ is doubtful. Since face-to-face interactions are not sterically hindered, the absence of intramolecular excimer formation in 1,3-bicarbazoly propane could therefore be a reflection of the electronic fluorescence properties of the carbazolyl moiety, rather than geometric restrictions.

The controversy over the involvement of neighboring and non-neighboring interactions in excimer formation in polymers becomes even more crucial in studies of fluorescent properties of copolymers. This is because the phenomenon of intramolecular excimer formation is potentially useful in understanding monomer sequence in copolymers.^{71,72} For example,⁶⁶ according to reactivity ratio, copolymer of 1-vinylnaphthalene and styrene would tend towards an alternating copolymer structure. The observance of intramolecular excimer fluorescence in the above copolymers, having as low as 3-4 mole percent vinylnaphthalene units, suggests that sequences of two or more adjacent units containing naphthyl groups must be dominant; otherwise, the excimers are formed between non-adjacent chromophores on the same chain. With the structure of the copolymer in question remaining uncertain, it is difficult to access the validity of either interpretation on the sequence of 1-vinylnaphthalene-styrene copolymer. Our polyamide series, with their well-defined copolymeric structures, seem to offer a useful system for distinguishing between adjacent and non-adjacent chromophoric interactions in a polymer chain. In addition, our studies may shed light on the general question of possible conformations of a 'giant' molecule in solution.

In this chapter, we will study the absorption and emission characteristics of the polyamide series: P2-14,

P4-14, P6-14 and P8-14, and the model compound 11 (their synthesis is described in Chapter 3). For brevity, we will re-designate these compounds as P-2, P-4, P-6 and P-3 and MC respectively.



We will present evidence for intramolecular excimer formation in the above polyamide series. Results of fluorescence lifetimes and quantum yield measurement of monomer and excimer emissions will be given. A kinetic and thermodynamic analysis of the temperature effect on excimer emission in P-2, will also be made. The influence of viscosity on intramolecular excimer interaction in P-2, will be discussed. Finally, evidence for the occurrence of 'dimer' emission at high polymer concentrations will be presented.

Absorption and Fluorescence Spectra of Polyamides and Model Compound

The room temperature absorption spectra of the monomer model compound (MC) and polymer, P-2, are shown in Figure 4.1. A dilute solution (1 x 10^{-4} M/L in CHCl₃/EtOH, 1:3) of each compound was used. The molarity of the polymer solution was based on the weight of the 'repeat unit'. The absorption spectra of the other polyamides: P-4, P-6 and P-8, were similarly obtained, and are identical to that of P-2. From the above figure, it is clear that the monomer model compound has the same absorption characteristics with the polymers; their molar extinction coefficients are similar (v5,000). Also, the diamine monomer-2,6-bis(N-methyl, methylamino)naphthalene(8), III possesses an identical absorption spectrum (Figure 6.1).

The absorption bands shown in Figure 4.1 are due to the naphthalene moiety. The weak, long-wave-length peaks: 308, 315 and 322 nm are due to the ${}^{1}L_{b}$ naphthalene transition; the intense peak, with an absorption maximum at ~275 nm, is due to the ${}^{1}L_{a}$ transitions. The identical absorption properties of the above compounds show that only weak ground state interactions involving the naphthalene chromophore occur in the polymer.

The room temperature fluorescence spectra of the model compound (MC) and the polyamides: P-2, P-4, P-6 and P-8, are shown in Figure 4.2. The model compound



Figure 4.1. Room temperature absorption spectra: a) Monomer model compound, b) P-2 (1 x 10^{-4} M in CHCl₃/EtOH, 1:3). λ_{ex} 290 nm.





shows only a single fluorescence emission band which is attributed to the naphthalene emission with a maximum (λ_{em}^{max}) at \sim 355 nm. In contrast, the polyamides show in addition to the naphthalene (monomer) fluorescence band at 355 nm, a broad band at longer wave lengths, (\sim 425 nm).

A number of questions immediately arise: what chemical species gives rise to the new band? What are the photophysical processes that lead to such band? It is relevant to note that the diamine monomer (8), III, shows a two-component fluorescence band (see Figure 6.3), under the same conditions used for obtaining the polymer fluorescence spectra. As will be discussed in Chapter 6, and according to a recent report⁷³ by the author, this broadband in the diamine spectrum is attributed to a solvent-induced intramolecular excited state complex (exciplex), formed between the naphthalene (acceptor) group and the amino (donor) group.

Thus it is natural to consider first the possibility of a donor-acceptor interaction occurring between the amide nitrogen and the naphthalene group, in the polymer backbone. However, a number of observations rule out such possibility:

i) the absence of a similar band in the fluorescence spectra of the monomer model compound (MC), which possesses the amide group similarly linked to the naphthalene group, as in the polyamides.

ii) the slight enhancement of the broad band in the polyamides upon addition of a few drops of trifluoroacetic acid; a similar treatment to a solution of the diamine (8), leads to a complete quenching of the broad emission band, with a considerable enhancement of the monomer (naphthalene) emission. This is due to protonation which ties up the nitrogen lone-pair electrons, thus increasing its ionization potential.

The next logical candidate for the broad emission band is the interaction between two naphthalene groups, either in the same or different polymer chains. The fact that dilute polymer solutions exhibit these broad bands suggests that the interaction is intramolecular. Further confirmation of this, which comes from concentration studies, will be presented later. The next question is whether the interaction occurs in the ground or excited state. If it is in the ground state, then it is a 'dimer' complex, which should exhibit some characteristic absorption band. Identical absorption spectra of the model compound and those of the polyamides rule out any significant ground state interaction between the naphthalene groups. The observed coincidence of the excitation spectra of the monomer emission at $\lambda_{\rm em}$ 355 nm and that of the broad band at λ_{pm} 425 nm strongly suggests an excited state interaction of the naphthalene moleties, and that the new broad band arises from an intramolecular naphthalene excimer.

Subsequent studies in this chapter will support this.

The slight enhancement of the excimer emission due to addition of acid can be accounted for in terms of the elimination of the small perturbation effect of the lonepair nitrogen of the amide group. Such perturbation effect in the amide monomer is small compared to the amine monomer due to the carbonyl group which reduces the basicity of the nitrogen. Thus, intramolecular excimer interaction versus intramolecular exciplex interaction is more favorable in the polyamide systems. Such an enhancement of excimer fluorescence in heterochain systems by protonation or acylation of the lone pair on a chain-nitrogen atom, has been reported by Wang and Morawetz⁷⁴ (1976). They found that di-benzylamine in its basic form, does not show any detectable fluorescence, while in the protonated or acylated form (as in N.N-dibenzylformamide) it exhibits a strong excimer band. In the basic form, it appears that the nitrogen lone pair, despite the intervening methylene group, effectively quenches the excited singlet state of the phenyl group, perhaps via an intramolecular exciplex mechanism. In this respect, the use of polyamides in studying intramolecular excimer formation in nitrogencontaining heterochain systems seems advantageous.

Kinetics of Intramclecular Excimer Formation

For a kinetic treatment of the photophysical processes involved in intramclecular excimer formation, we draw the following reaction scheme, which is similar to the intermclecular case, $3^{9,75}$ except that the rate constant of association is of first order:



where M represents the monomer (in our case - naphthalene) and D* is the intramolecular excimer. Birks,⁷⁶ nomenclature is used for the monomer and excimer rate constants, which are defined as follows:

- $k_{\rm FM}$: fluorescence of monomer
- \mathbf{k}_{TM} : internal quenching of monomer
- k_{DM} : excimer formation
- \mathbf{k}_{FD} : fluorescence of excimer
- \mathbf{k}_{MD} : dissociation of excimer
- k_{TD} : internal quenching of excimer

For simplified analysis, we also define the following parameters,

$$k_{M} = k_{FM} + k_{IM}$$

 $k_{D} = k_{FD} + k_{ID}$

If the system is subjected to steady excitation with light intensity I_0 einsteins $l^{-1}s^{-1}$, the rate equations are:

$$\frac{d[^{1}M^{*}]}{dt} = I_{o} - (k_{M} + k_{DM})[^{1}M^{*}] + k_{MD}[^{1}D^{*}]$$
(4.1)

$$\frac{d[^{l}D^{*}]}{dt} = k_{DM}[^{l}M^{*}] - (k_{D} + k_{MD})[^{l}D^{*}]$$
(4.2)

Assuming photostationary conditions

$$\frac{d[^{l}M^{*}]}{dt} = \frac{d[^{l}D^{*}]}{dt} = 0$$

then

$$[^{1}M^{*}]_{stat} = \frac{I_{o}(k_{D}+k_{MD})}{(k_{D}+k_{MD})+k_{M}+k_{D}k_{DM}}$$
(4.3)

$$[^{1}D^{*}]_{stat} = \frac{I_{o}k_{DM}}{(k_{D}+k_{MD})+k_{M}+k_{D}k_{DM}}$$
(4.4)

The intensity of monomer fluorescence (photons per unit time) is given by

$$I_{M} = k[^{1}M^{*}]k_{FM} \qquad (4.5)$$

where k is a constant, dependent on the experimental conditions. Similarly, excimer fluorescence intensity is given by,

$$I_{D} = k[^{1}D*]k_{FD} \qquad (4.6)$$

Substituting for $[^{1}M*]$ and $[^{1}D*]$ in equations (4.3) and (4.4), using Equations (4.5) and (4.6) respectively, the ratio of the excimer fluorescence intensity to that of the monomer, becomes:

$$\frac{I_D}{I_M} = \frac{k_{\rm FD}k_{\rm DM}}{k_{\rm FM}(k_{\rm D}+k_{\rm MD})}$$
(4.7)

The corresponding experimental decay times are given by:

$$\tau_{\rm M} = (k_{\rm FM} + k_{\rm IM})^{-1}$$
 (4.8)

$$\tau_{\rm D} = (k_{\rm FD} + k_{\rm ID})^{-1}$$
(4.9)

The above relations will be utilized in the following sections to obtain kinetic and thermodynamic parameters for excimer formation in the polyamides and model compound.

Fluorescence Quantum Yields, Decay Times and Rate Constants of Polyamides and Model Compound

Decay times for monomer and excimer fluorescence were determined by single photon counting technique using a nanosecond time-resolved spectrometer. Solutions of the polyamides and model compound (2 x 10^{-4} M/L in CHCl₃/ EtOH, 1:3) degassed by a three-cycle freeze-pump-thaw, were used; all measurements were done at room temperature. Monomer and excimer decay data were monitored at 330 nm and 425 nm respectively and are shown in Figure 4.3. These decay curves provide⁷⁷ a graphic demonstration of the reality of the excimer formation process. Similar decay patterns were obtained for the other polyamides.

Analysis of lifetime data was done by KINFIT to obtain the experimental decay times for monomer (τ_M) and excimer (τ_D) emissions, and the corresponding rate constants k_M and k_D . These results, along with the calculated rate constants for fluorescence emission of monomer (k_{FM}) and excimer (k_{FD}) are shown in Table 4.1. Calculation of k_{FM} or k_{FD} was done using the relation:

$$k_{FM} = \tau_M / \Phi_{FM}$$

where $\Phi_{\rm FM}$ is the monomer fluorescence quantum yield. Relative fluorescence quantum yields of monomer and excimer



Figure 4.3. Fluorescence Decay curves of P-4: Top-monomer $(\lambda_{\rm em}~330~{\rm nm}):~{\rm bottom-excimer}~(\lambda_{\rm em}~425~{\rm nm}).$

Fluorescence Quantum Yields ($^{\Phi}$), Decay Times (T) and Rate Constants (k) of Polyamides and Model Compound (1 x 10⁻⁴ M in CHCl₃EtOH, 1:3). Table 4.1.

				Monomer				Excimer	
Compound	ᆄ <mark>ᅴ</mark> ᆤ	ф _{РМ}	T _M (nsec)	k _M (10 ⁷ sec ⁻¹)	^k FM (10 ⁶ вес ⁻¹	Φ_{FD}	τ _D (nsec)	k _D (10 ⁷ هور ⁻¹)	k _{FD} (10 ⁵ sec ⁻¹)
Model CPD		0.146	28.49	3.51	5.10				
P-2	0.19	0.112	25.77	3.88	4.40	0.021	35.21	2.84	6.00
P-4	0.12	0.143	27.93	3.58	5.12	0.017	48.54	2.06	3.50
P-6	0.11	0.153	29.07	3.44	5.30	0.017	36.23	2.76	4.70
P-8	0.16	0.147	27.70	3.61	5.30	0.023	45.25	2.21	5.10

were obtained using 2,6-dimethylnaphthalene as a standard. Undegassed solutions (1 x 10^{-4} M/L in CHCl₃/EtOH, 1:3) were used. Results are presented in Table 4.1, along with ratios of fluorescence intensities of monomer and excimer, (I_D/I_M). A plot of excimer fluorescence quantum yield, Φ_{FD} and I_D/I_M ratio, versus the number of atoms (n) in the chain between naphthyl groups, is given in Figure 4.4. A minimum in both Φ_{FD} and I_D/I_M is observed at n=10 and 12 (representing 20, 2N, 6C and 20, 2N, 8C atoms respectively); while maximum values of Φ_{FD} and I_D/I_M occur at n=8 and 14 (representing 20, 2N, 4C and 20, 2N, 10C, respectively). These trends are also reflected in the fluorescence spectra (Figure 4.2).

Activation Energy for Excimer Formation in Polymer, P-2

Intramolecular excimer formation, like the intermolecular case, is a diffusion-controlled process. However, unlike the intermolecular case, the binding of the two interacting chromophores by a chain (as in composite or polymeric systems) removes any effects on excimer interaction, due to molecular translational diffusion; thus the main dynamic influence would appear to be due to molecular rotation. In polymeric systems, an additional molecular motion comes into effect, namely microbrownian (segmental) motion, and it appears to be a major determining factor in intramolecular excimer formation in




polymers.

In order to examine the above dynamic effects, the fluorescence emission of P-2 was taken at different temperatures (Figure 4.5). A maximum in the excimer fluorescence intensity is evident at -16.5°, decreasing above and below this temperature. On the other hand, monomer fluorescence intensity increases continuously with decrease in temperature.

The activation energy for intramolecular excimer formation in P-2 was computed using Equation 4.7,

$$\frac{I_{D}}{I_{M}} = \frac{k_{FD}k_{DM}}{k_{FM}(k_{D}+k_{MD})}$$

The following assumptions were made:

i) k_{FD} and k_{FM} are independent of temperature. ii) $k_{MD} \ll k_D$ (in the low temperature region). iii) $k_{MD} \gg k_D$ (in the high temperature region).

Assumption (i) generally holds over a wide range of temperatures for many aromatic molecules.⁷⁸

Using assumption (ii), then at low temperature

$$\frac{I_{\rm D}}{I_{\rm M}} \approx \frac{k_{\rm DM}}{k_{\rm FM}}$$

Since k_{DM} represents an activated process (excimer formation) we can replace it with the Arrhenius relation to



Figure 4.5. Temperature dependence of intramolecular excimer emission in polymer, P-2: _____ 21.5, _______16.5,_62.3, _______110°C. Sol-_____vent: chloroform-ethanol (1:3); λ_{ex} 290 nm.

obtain

$$ln(\frac{I_D}{I_M}) = ln \frac{1}{k_{\rm FM}} - \frac{E_D}{RT}$$
(4.10)

where E_D is the activation energy for intramolecular excimer formation. A plot of $\ln\left(\frac{I_D}{I_M}\right)$ versus T^{-1} for P-2 gave a straight line, in the low temperature region, with a negative slope (Figure 4.6), thus validating assumption (ii) above. From the slope, which is equal to $\left(-\frac{E_D}{R}\right)$, an activation energy of 1.8 kcals mole⁻¹ was obtained.

Under assumption (iii), we get that

$$\ln(\frac{I_{D}}{I_{M}}) = \ln(\frac{k_{FD}}{k_{FM}}) + \ln(\frac{k_{DM}}{k_{MD}})$$
$$= \frac{(\Delta H_{MD}^{\neq} - \Delta H_{DM}^{\neq})}{RT} - \frac{(\Delta S_{MD}^{\neq} - \Delta S_{DM}^{\neq})}{R} + \text{constant} \qquad (4.11)$$

where $(\Delta H_{MD}^{\neq} - \Delta H_{DM}^{\neq})$ is the enthalpy change of the monomerexcimer equilibrium. A plot of $\ln(\frac{I_D}{I_M})$ versus T^{-1} for P-2 gave a straight line in the high temperature region, with positive slope (Figure 4.6). From the slope, a value of 2.2 kcal mole⁻¹ was obtained for $(\Delta H_{MD}^{\neq} - \Delta H_{DM}^{\neq})$.

Discussion

We will now discuss the foregoing results of fluorescence lifetime, quantum yield and activation energy measurements. First, we examine the structural basis for the





formation of intramolecular excimers in the polyamides:

For purposes of illustration, we consider one of the polyamides, P-2, represented above in its fully extended form. In this model (Fisher-Herschfelder-Staurt's), the methylene chain of the dicarboxylic acid moiety, is planar zigzag and coplanar with the amide linkage.⁷⁹ The plane of the naphthalene ring is then perpendicular to that of the amide group, in order to minimize steric interaction between the hydrogen atoms of the ring and those on the methylene groups attached to the ring.

Rotation about the C-N bond of the amide group is hindered because of its partial double bond character. This introduces rigidity in the chain, likewise the presence of the naphthalene ring impacts additional rigidity. However, molecular rotation is possible about the following bonds: $C_{ar}-C_{al}$, $C_{al}-N$, and $C_{al}-C_{al}$) (al-aliphatic and ar-aromatic). Thus, the naphthyl ring can rotate about the axis that link it to the two methylene carbon atoms;

this motion seems to occur extremely fast, with a relaxation time on the order of 10^{-9} sec. Evidence for this. comes from fluorescence depolarization measurements (Figure 4.7), in which the parallel and the perpendicular components of the polarized monomer fluorescence have equal decay times. This implies that some rotational motion of the polymer chain, involving the ring, has a relaxation time greater than the excited state lifetime of the naphthalene moiety (i.e., 10^{-9} seconds). Since it is unlikely that the entire repeat unit would execute a segmental motion that fast, it seems reasonable to attribute the observed complete fluorescence depolarization in these polyamides to the free and fast rotation of the ring about the axis that links it with the two methylene groups; with the amide groups serving as 'hinges'. In addition, there is free rotation of the methylene chain (of the carboxylic acid moiety). Consequently, the combined effect of the two motions: ring and methylene chain rotations, would render the polyamides flexible.

In dilute solution, such a flexible polymer molecule, exists in the form of a contorted coil, continuously changing its shape. During these writhings of the polymer chain, long-range forces (dipole-dipole, dipole-induced dipole and dispersion forces) can lead to the approach to one another, of groups that are distantly located on the chain. Such interactions are expected to be pronounced in polyamides



Figure 4.7. Fluorescence depolarization: top, P-2, bottom, P-8.

where the amide functional groups bear large dipole moments (3.7 Debye)⁸⁰ directed approximately perpendicular to the chain axis. Thus, intramolecular excimer formation in polymers like ours, that possess widely separated chromophores, would rest largely on the flexible, coiling nature of the chain.

The observation that the fluorescence quantum yields of the intramolecular excimers in the polyamides show a maximum at n=8 and 14, and a minimum at n=10 and 12, may be rationalized as follows: We propose that intramolecular excimer interaction in these polyamides can occur between neighboring naphthyl groups and/or non-neighboring ones. Under this premise, the maximum at n=8 (P-2) is probably due to the relatively greater frequency of encounter between neighboring naphthyl groups, because of the shorter distance of separation. As we go to P-4, the increased distance of separation reduces the rate of encounter between neighboring naphthyl groups; so that its excimer fluorescence may arise largely from non-neighboring interactions (Figure 4.8a). The fraction of such non-neighboring excimer sites seems to be small, hence the observed decrease in excimer fluorescence intensity. The same effect appears to be operating in P-6 also. However, as the chain becomes considerably long as in P-8, the flexibilizing effect of the methylene chain can lead to loops, in which neighboring naphthyl groups are once more brought into close proximity



Figure 4.8. Non-neighboring and neighboring group interactions, a) and b) respectively. Solvent effect on polymer conformation: compact coil in poor solvent (a and b), expanded coil in good solvent (c).

(Figure 4.8b), resulting in the observed increase in excimer fluorescence intensity.

Evidence in favor of the involvement of non-neighboring naphthyl groups in intramolecular excimer formation, is provided by a strong solvent effect on excimer fluorescence in P-4 (Figure 4.9). The intensity of excimer emission is seen to be least in $CHCl_3$ (thermodynamically good solvent) and highest in $CHCl_3/EtOH$, 1:3 (thermodynamically poor solvent). In a good solvent, the polymer chain will be highly expanded (Figure 4.8c), thus substantially reducing the number of excimer-forming sites. But in a poor solvent, the polymer chain assumes a compact conformation (Figure 4.8a), thus permitting non-neighboring-group interactions, with an increase in excimer fluorescence.

The difference in the decay times of excimer emissions in the P-2, P-4, P-8 excimers (35, 48 and 45 nsec, respectively) may reflect the predominant neighboring naphthalene interactions in the P-2 polymer. The smaller lifetime may be rationalized in terms of a less symmetric excimer.

The activation energy of $1.8 \text{ kcals} \cdot \text{mole}^{-1}$ obtained for P-2, is comparable to those reported for poly(1-viny1naphthalene) and poly(2-vinylnaphthalene):⁶⁶ 2.1 and 2.0 kcals mole⁻¹, respectively. Also, activation energies on this order of magnitude were reported for a series of polyesters possessing widely-separated pendant naphthyl





groups.³⁷ In contrast, 1,3-di(l-naphthyl)propane and 1,3-di(2-naphthyl)propane have the following activation energies: 3.3 and 4.5 kcals mole⁻¹ respectively. One wonders why these smaller molecules would possess higher activation energies for intramolecular excimer formation. Two factors may be considered responsible for this:

i) availability of more favorable conformations to adjacent or non-adjacent chromophores due to chain coiling.

ii) possible energy transfer along the chain, with a favorable conformation for excimer formation acting as a sink.

The above factors, notwithstanding, measured activation energies for intramolecular excimer formation in polymeric systems should also reflect the degree of segmental diffusion. The closeness in activation energies between the above vinyl-polymers (with pendant naphthyl groups) and P-2 (with doubly-bound naphthyl groups) seems to imply that our polyamides are equally as flexible, despite the presence of the amide group and doubly-bonded, chainincorporated aromatic rings.

In this respect, it is pertinent to note that Hayashi and Tazuke³⁶ (1973) did not detect intramolecular excimer fluorescence in the following series of polyamides:



In this series, as in ours, the fluorescent aromatic moiety is doubly-bonded in the polymer chain; also the same series of aliphatic dicarboxylic acid groups are involved. However, their polyamides appear to be poor candidates for intramolecular excimer interaction because of a number of disabilities:

i) Increased chain rigidity resulting from the conjugation of the carbonyl groups with the carbazolyl groups; this would tend to lead to more extended linear chains in dilute solution.

ii) Hydrogen bonding of the amide groups causes further rigidity, and makes the polymers very insoluble in solvents suitable for fluorescence studies; and

iii) The carbazolyl group itself is a poor excimerforming aromatic species; for example, intermolecular excimers of N-isopropyl carbazole are not observed at all,⁸² and it has been suggested that the weak excimer-type emission in 1,3-dicarbazolyl propane (which satisfies "n=3 rule") may be due to an intramolecular dimer.⁶⁵ Thus, in view of the above chemical and structural disadvantages, it is therefore not surprising that the polyamide series having the carbazolyl unit in the backbone, failed to show intramolecular excimer fluorescence.

Effect of Viscosity on Excimer Formation in Polymer, P-2

Intramolecular excimer formation in polymeric systems, as noted in the preceding section, proceeds via chain conformational transitions, the rate of which is related to the internal viscosity, ϕ , of the polymer chain. Internal viscosity of a polymer chain can be defined as the ratio of a force applied to the ends of the chain to the rate of their separation, when the chain is suspended in a medium of negligible viscosity. Originally, ϕ was thought to be independent of the viscosity of the medium. However, it is now believed to consist of two components: ϕ' and ϕ ". ϕ ' is the potential barrier separating the chain conformations; this component is independent of the viscosity of the solvent. ϕ " arises from the lateral displacement through the viscous medium of chain elements next to the location of conformational change; and so it is dependent on solvent viscosity (η) . The following empirical relation has been found to hold:

$$\frac{\Phi}{f\eta} = \frac{A}{\eta} + B \qquad (4.12)$$

where f is the friction coefficient of a segment. From our earlier consideration of the rate processes involved in intramolecular excimer formation, we obtained Equation (4.7), which can be re-written as,

$$\frac{I_{M}}{I_{D}} = \frac{k_{FM}(k_{D} + k_{MD})}{k_{FD} k_{DM}}$$
(4.13)

In Equation (4.13), the viscosity dependent terms are k_{MD} and k_{DM} . If $k_D >> k_{MD}$, then $\frac{I_M}{I_D}$ is proportional to $\frac{1}{k_{DM}}$. But k_{DM} is the rate constant for a conformational transition involved in excimer formation, so that $\frac{I_M}{I_D}$ is expected to be linearly related to the medium viscosity.

To verify the linearity of the above relation, fluorescence spectral measurements were carried out at room temperature, using dilute solutions (1 x 10^{-4} M/L) of P-2, in a mixture of chloroform, ethanol and glycerol. The amount of chloroform was kept constant at 25% by volume; while the amounts of ethanol and glycerol were varied up to a maximum of 45% by volume of glycerol. Higher amounts of glycerol could not be used without precipitating the polymer from solution. The fluorescence spectra obtained are given in Figure 4.10.

At low viscosities (\leq 10 cp) the intensity of the excimer band appears constant, while the monomer band increases with increase in medium viscosity. A plot of $\frac{I_M}{I_D}$ versus viscosity (η) of medium is given in Figure 4.11. There is linearity in the plot at moderate viscosities, and curvature at low viscosities. Similar results were







reported by Avouris et al.,⁸⁴ for 1,3-dinaphthylpropane. On the other hand, Wang and Morawetz⁷⁴ obtained a linear plot for di-benzylether, at both low and high viscosities. The non-linearity in our system at low viscosities may be due to the assumption: $k_D >> k_{MD}$, which is not quite correct for P-2 at room temperature, at which the fluorescence spectral measurements were made, at different viscosities. This is because, $\frac{I_D}{I_M}$ in P-2, decreases with rise in temperature in the vicinity of room temperature, so that k_{MD} (rate constant for excimer dissociation) is likely to be competitive.

However, the behavior of monomer and excimer fluorescence in P-2 at low and moderate viscosities indicate a number of things:

 insensitivity of chain conformational transitions to low macroscopic viscosities, as shown by the constant intensity of the excimer band in this region;

ii) the linear dependence of $\frac{I_M}{I_D}$ on medium viscosity at moderate viscosities, and its finite value at zero viscosity, tend to support the concept of chain internal viscosity as a sum of two terms: a viscosity-dependent and a viscosity-independent term;

iii) the enhancement of monomer fluorescence even at very low viscosities seems to show substantial slowing down of molecular collision around the excited chromophores, which would lead to a decrease in thermally-induced radiationless processes, and hence, enhancement of fluorescence.

'Dimer' Fluorescence at High Polymer Concentration

'Dimers' are ground state complexes formed by a reversible combination of two unexcited monomer molecules (see classification of molecular complexes, Table 1.1). They occur frequently in concentrated solutions of many dye stuffs, and lead to a change in the shape of the absorption spectrum of the monomer compound. Dimer formation, in the ground state, has not been reported in concentrated solutions of neutral, small aromatic hydrocarbons like benzene, naphthalene and pyrene, at room temperature.

However, some workers have indicated the formation of dimers in concentrated solutions of some polymers. Nishihara and Kaneko⁸⁵ (1969) showed the existence of dimers in concentrated solutions of polystyrene, by the change in shape of the excitation spectra at different concentrations; Tazuke and Banba³⁷ (1976) alluded to dimer formation in concentrated solutions of a polyester containing pendant naphthylmethyl groups. Both studies did not show any detectable dimer fluorescence. To date, the only report, to our knowledge, on dimer fluorescence in concentrated polymer solution, is that of Kaniijo et al.⁸⁶ (1976) on polyvinylnaphthalene, which fluoresces, peaking at 342, 360 and 378 nm. In attempting to establish the concentration independence, and the intramolecular nature of excimer formation in our polyamides, we have observed a third peak, at higher energy than excimer emission. Solutions of P-2, P-4 and model compound were prepared in a 1:1 mixture of CHCl₃ and ethanol, with concentrations ranging from 1 x 10^{-6} to 1 x 10^{-1} M/L. All solutions were used undegassed. Fluorescence and excitation spectra were obtained in 1 cm cell, by right-angle viewing.

Effect of Concentration on Fluorescence Spectra of P-2

Though similar spectral characteristics were obtained for P-2, P-4 and MC, those of P-2 are by far more dramatic, followed by P-4. A detailed account of the behavior of P-2 is thus given, and similarities and differences between its behavior and those of P-4 and MC will be pointed out. Spectral measurements on P-2 at room temperature and at different concentrations reveal three types of behavior, depending on the concentration (Figure 4.12).

i) High dilution region (<10⁻⁵ M/L). The ratio of intensities of excimer and monomer fluorescence, $\frac{I_D}{I_M}$, increases with decrease in concentration.

ii) Moderate dilution region (4 x $10^{-5} - 1 x 10^{-3}$ M/L) $\frac{I_D}{I_M}$ ratio is independent of concentration. iii) High concentration region ($\sim 2 \times 10^{-3} - 1 \times 10^{-1}$ M/L).





Fluorescence spectra in this region are shown in Figure 4.13. The following observations are made:

continuous decrease in monomer (naphthalene) fluorescence (λ_{em} 362 nm) with increase in concentration; complete quenching occurs at $\sim 1 \times 10^{-1}$ M.

the broad excimer peak $(\lambda_{em}^{max} \sim 428 \text{ nm})$ increases proportionally with increase in concentration, and shifts to the red by $\sim 22 \text{ nm}$.

appearance of a new peak at 380 nm, which begins at $\sim 2 \times 10^{-3}$ M/L, and grows with increase in concentration.

Fluorescence Spectra of P-2 at Varying Excitation Wavelengths

A dilute solution $(2 \times 10^{-4} \text{ M/L})$ and a concentrated solution $(2 \times 10^{-2} \text{ M/L})$ of P-2 in 1:1 mixture of CHCl₃ and ethanol were excited at different wavelengths (294-324 nm) at room temperature. The behavior of the two solutions are markedly different. Dilute solution (Figure 4.14a):

the total fluorescence spectra shows no change in shape. monomer fluorescence has maximum intensity at λ_{ex} 294 nm, and decreases by a factor of ~5.6 at λ_{ex} 324 nm.

Concentrated solution (Figure 4.14b):

the total fluorescence band shows a change in shape:







the new band showing a higher peak height at λ_{ex} 294 nm than at λ_{ex} 324 nm; the reverse is the case for the monomer band.

the ratio of intensities of excimer to monomer fluorescence, $\frac{I_D}{I_M}$, increases with decrease in wavelength (Figure 4.17).

Excitation Spectra of P-2

The excitation spectra of the two solutions of P-2 used in the preceding section, were recorded at room temperature. The emission monochromator was set at λ_{em} 362 and 380 nm, to obtain the excitation spectra of the monomer and the new-peak 'species', respectively. The following observations are made (Figure 4.15):

in both dilute and concentrated solutions, the excitation spectra at $\lambda_{\rm em}$ 362 nm and $\lambda_{\rm em}$ 380 nm are coincident.

excitation spectra of concentrated solution are, however, sharper, and with a short wavelength tail (Figure 4.15a).

also, excitation band of the concentrated solution has a maximum at λ_{ex} 325 nm, and that of the dilute solution is at λ_{ex} 292 nm.





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Effect of Concentration on Fluorescence Spectra of P-4 and MC

Spectral measurements, with concentrated solutions of P-4 and model compound (MC) were also made at room temperature in a 1:1 mixture of $CHCl_3$ and ethanol. Their fluorescent behavior under the same conditions are then compared with those of P-2, at a particular concentration (2.5 x 10^{-2} M/L) and at excitation wavelengths - 290 and 324 nm (Figure 4.16). Significant similarities and differences are observed:

the fluorescence of MC is practically quenched when excited at 290 nm; however, on excitation at 324 nm, it shows detectable monomer fluorescence, and with the new component at ~ 380 nm.

the fluorescent behavior of P-4 as a function of concentration, is very similar to that of P-2, with two exceptions:

the intensity of the new peak at 380 nm is less in P-4, at equivalent concentrations.

 $\frac{-D}{I_{M}}$ ratio decreases with increase in excitation wavelength in P-2; the reverse is the case in P-4 (Figure 4.17).



Figure 4.16. Comparison of fluorescence spectra of concentrated solutions (2.5 x 10⁻² M/L) of polyamides (P-2, P-4) and model compound (MC): ---- MC (λ_{ex} 324 nm), ---- P-4 (λ_{ex} 324 nm) \dots P-4 (λ_{ex} 290 nm), ---- P-2 (λ_{ex} 290 nm).



Discussion

The initial goal for carrying out the spectral measurements with solutions of P-2 and P-4 at different concentrations was to establish the intramolecular nature of excimer formation in them and the other members of the series. A plot of $\frac{I_D}{I_M}$ versus concentration, is seen to be invariant with concentration in the moderately dilute region; thus, confirming the occurrence of excimer interaction between naphthyl groups of the same chain. The reason for the increase in $\frac{I_D}{I_M}$ ratio with decrease in concentration in the extremely dilute region (1 x 10⁻⁵ M/L), is not totally clear at this point, although it seems to reflect some increased ease of chain conformational transitions, made possible by better isolation of each polymer chain at such extreme dilutions.

We now proceed to explain the fluorescent behavior of P-2, P-4 and model compound at high concentrations. The observed increase in $\frac{I_D}{I_M}$ ratio with increase in concentration conforms to the behavior of small aromatic hydrocarbons. At high concentrations, quenching of excited singlet aromatic moieties by their ground state counterpart, occurs; leading in most cases, to the formation of intermolecular excimers. But unlike the case of small aromatic hydrocarbons, concentrated solutions of P-2, P-4 and even the model compound, showed a new peak at 380 nm, which lies to the blue of excimer fluorescence. This implies the existence of a third emitting species, and more than one absorbing species. The presence of a second absorbing species is also indicated by the observed change in shape of fluorescence spectra on varying the excitation wavelength. This is even further confirmed by the shift to longer wavelength (325 nm) of excitation maximum at high concentration (P-2, Figure 4.15), together with a change in shape of the excitation spectra.

We therefore believe that at high concentrations, 'dimers' of naphthalene moieties are formed, which fluoresce at 380 nm. The absorption and emission properties of paracyclophanes, with two benzene rings bridged by $(CH_2)_m$ and $(CH_2)_n$ groups, illustrate this type of ground-state, proximity-induced interaction. For example, ¹⁶ 2,2'-paracyclophane shows absorption maximum (λ_{ab}^{max}) at ~ 282 nm, and emission maximum (λ_{em}^{max} at 356 nm; while 4,4'-paracyclophane shows λ_{ab}^{\max} at 261 nm and λ_{em}^{\max} at 335 nm. The emission bands in both compounds are due to intramolecular The absorption and emission spectra of 4, 4'excimers. paracyclophane are similar to those of a dilute solution of polystyrene, which in turn has an absorption spectrum similar to that of ethylbenzene. Thus, it is seen that in 2,2'-paracyclophane, there has been a shift to the red in both the absorption maximum and in excimer emission The above differences are attributed to the maximum. intermolecular electronic interactions of the phenyl

groups in their ground states because of the proximity of the two chromophores in 2,2'-paracyclophane. We invoke the same reasoning to explain our observations in concentrated solutions of the polyamides, namely the shifts to the red of both the excitation maximum and the excimer emission maximum. Concentrated solutions of polystyrene, as noted earlier, exhibit similar red shifts in its excitation and excimer bands; this behavior was similarly rationalized.⁸⁵

The contrast in the fluorescence behavior of P-2, P-4 and MC may be explained in terms of the following qualitative scheme:



Dimer formation between the naphthalene moieties in concentrated solutions, is considered to arise from enhanced dipole-dipole, dipole-induced dipole and dispersion interactions due to the close proximity of the naphthalene groups. These dimers on excitation (process 4) can undergo a number of processes:

i) fluoresce at $\lambda_{em} \sim 380$ nm (process 12);

ii) form an excimer, a much more stable excited complex (process 7);

iii) dissociate into an excited monomer and a ground state monomer (process 5).

Generally, excited dimers do not fluoresce because of their small enthalpy (- Δ H) of formation, which when less than RT, would lead to rapid dissociation of the excited dimer. This might be the case in polystyrene dimers, for which no detectable fluorescence was reported.⁸⁵ However, in our polyamides, the presence of the amide dipoles in the chain, would give rise to a relatively stronger intra and interchain secondary (dimeric) interactions, leading to the formation of stable excited dimers with characteristic emission at 380 nm. Dimers of the model compound, however, appear less stable, because of the absence of the 'locking effect' of the polymer chain, which would tend to hold the interacting naphthyl groups in place, and in a more or less stable conformation that will permit effective exciton resonance between them. On the other hand, the fluorescence intensity of the dimer of P-4 is less intense than that of P-2 because of 'dilution effect', caused by larger average distance of separation of naphthyl groups in the former polymer, in which there will be smaller density of chromophores for the same moles of repeating units.

Because of the above 'locking effect' in polymeric systems, it seems conceivable that excited dimers may also be formed via process 6, in which there is strong exciton coupling between an excited monomer and a ground state monomer. Two experimental observations appear to support the above suggestion: the coincidence of the excitation spectra of monomer and dimer fluorescence monitored at 362 and 380 nm respectively; thus suggesting the involvement of excited singlet state of naphthalene in dimer formation. Also the observed higher intensity of dimer fluorescence upon excitation at ~290 nm (monomer absorption maximum) suggests that process 6 in the scheme may be efficient. However, the monomer and over-all fluorescence intensity is higher on excitation at longer wavelength (324 nm), which tends to support the existence of another absorbing species, which may dissociate to give excited monomers - in other words, processes 1, 4 and 5 may be predominant at long wavelength excitation at high concentrations.

Conclusions

We have demonstrated experimentally, the formation of fluorescent intramolecular excimers in a series of Nmethylated polyamides, with doubly bonded naphthyl groups in the backbone, separated from one another by as many as 20, 2N and 10C atoms. The fluorescence lifetimes and quantum yields of the excimers depend on the distance of separation between the chromophores, in a manner that seems to imply the involvement of non-neighboring groups in excimer interactions. Temperature measurements reveal a small energy requirement for the conformational transitions involved in the formation of these excimers; and limited viscosity studies indicate the extent the above transitions are dependent on the viscosity of the medium. Finally. we presented experimental evidence for the formation of fluorescent dimers in concentrated solutions of the polyamides and their model compound.

From the above findings, we can reach the following conclusions:

i) For a given aromatic moiety, intramolecular excimer formation can occur over long distances of separation between the chromophores, if the intervening chain is flexible.

ii) polyamides present an example of flexible hetero-chain systems that exhibit intramolecular excimer formation.Our work is however the first known case.

iii) Chromophores, doubly-bonded in a chain appear capable of engaging in intramolecular excimeric interactions; this is the first known case in polymeric systems.

iv) The 'n=3 rule, in its original statement, is no longer valid; rewording it as follows, seems necessary: "intramolecular excimer formation is <u>optimized</u> when the two interacting aromatic moieties are separated by a threeatom chain". In such a way the statement finds wide spread validity in homo and heterochain systems, the nature of the fluorescent moiety, notwithstanding.

v) Finally, the detection of dimer fluorescence in concentrated solutions of the polyamides and model compound suggests strongly the need to consider dimer formation in these systems.
CHAPTER 5

INTERMOLECULAR EXCIPLEX FORMATION IN POLYAMIDES HAVING NAPHTHYL GROUPS IN THE BACKBONE

Introduction

The binding of a chemical moiety in a polymer chain can lead to changes in its chemical or physical reactivity, Such changes, which may be termed, "polymer effect", contrast the behavior of the moiety in a monomeric and a polymeric situation. Rates of small molecule reactions have been accurately described in terms of collision theory and molecular dynamics. However, when polymers are involved, the concept of "billiard ball" collisions between molecules of nearly the same size, is no longer applicable. In solution, swollen or molten state of a polymer, the random motion of the billiard balls is replaced by a more restricted and coordinated motion. This drastic change in molecular notion, brought about by the steric restrictions of the chain, is likely to affect the reactivity of a moiety. For excimer or exciplex formation, the polymer effect will depend on the degree of movement of moieties needed to attain a given geometry during the excited state lifetime of a specific chromophore.

The phenomenon of intramolecular excimer formation, which we studied in the preceding chapter might be

considered a classic example of 'polymer effect', in which chain binding of chromophores leads to the observance of excimer fluorescence in dilute solution. Intermolecular excimer formation between similar chromophores occurs at higher concentration and is concentration dependent. Also, the same chain - binding determines as we saw earlier, to what extent intramolecular excimeric interactions can take place, between bound chromophores.

On the other hand, some reports have shown that, in certain intramolecular processes, the reactivity of a functional group remains essentially the same both in the monomeric and polymeric states. For example, Y. Miron⁸⁷ (1969), showed that the free energy of activation, ΔG_c^{\neq} for the rotation around the amide bond in piperazine, at the covalescence temperature, was almost identical for the piperazine polyamides and their low molecular weight analogs. Also, Tobak and Morawetz⁸⁸ (1970) reported that the isomerization rate of the azobenzene moiety is not significantly impeded by incorporation into the polymer backbone.

In the above intramolecular processes, however, rotational (segmental) motion is probably all that is required to bring about the necessary interactions; so that under these circumstances, any effect due to chain translatory motion, will not be evident. And, as a matter of fact, the binding of a molecular species in a polymer

chain literally removes its ability to do any sustained translatory motion, unless by a whole-molecule motion of the polymer, which hardly occurs.

Therefore, in order to get a total picture of polymer effect on the reactivity of a molecular moiety, it becomes useful to carry out intermolecular interactions involving polymers and their monomer model compounds. By so doing, the chain effect on both the translatory and rotational molecular motions, may become fully exposed. In choosing a reaction for this type of comparative study, an important criterion is that the reaction does not lead to any permanent changes in the electronic and physical states of the polymer or its monomer model compound. In this respect, photophysical processes have proved to be potentially useful. Three main approaches, involving the use of spectrophotometry have been reported in the literature:

In one approach, the absorption characteristics of ground state charge transfer (CT) complexes of polymers are compared with those of monomer model compounds. Equilibrium constants and molecular extinction coefficients of the CT complexes are determined using the Benesi and Hildebrand⁸⁹ relation which, for the case of excess donor concentration, is given by

$$\ell[A]/OD = 1/\epsilon_{CT} + 1/\epsilon_{CT}K[D]$$
(5.1)

where [A] and [D] are concentrations of acceptor and donor in moles/litre; OD is the optical density; $\epsilon_{\rm CT}^{}$ is the molar extinction coefficient of the complex, and K is its equilibrium constant in litre mole⁻¹. Results of some works based on this approach are not completely in agreement: Sugiyama and Kamogawa⁹⁰ (1966) studied CT complexes of aza-polymers (for example, poly-2-vinylpyridine and poly-4-vinyl pyridine) with guinone (acceptor) and the corresponding complexes of some monomer model compounds (for example, pyridine and methyl-substituted pyridines). They reported higher equilibrium constants for polymer complexes than for monomer complexes. They reasoned that, even though a longer period is required for quinone to approach the donor group of the polymer, the complex, once formed, is not so easily dissociated. Contrasting results were obtained by Rembaum et al^{91} (1968), when they studied CT complexes of poly(N-vinyl carbazole) and N-ethyl carbazole, with acceptors such as iodine and tetracyanoethylene. They obtained higher equilibrium constants for monomer complexes than for polymer complexes. They rationalized their results in terms of steric hinderance caused by chain configuration. The situation became even more confused with the results of Hayashi and Tazuke 36 (1973), who studied CT complexes of a series of polyamides having carbazole units in the backbone, and that of N-ethylcarbazole, using trinitrobenzene (TNB) as acceptor. They

reported higher equilibrium constant (K) for ethyl carbazole complex than for corresponding polymer complexes (in agreement with the results of Rembaum et al). On the other hand, higher K values were obtained for polymer complexes than for that of the monomer model compound, (EtCONH)₂Cz. They attributed the latter result to a possible aggregation of carbazole groups in the polymers, which could lead to a difference in the donor strength of the carbazole moiety. They did not explain why the monomer model compound, (EtCONH)₂Cz, exhibits less exciplex interaction with TNB compared with N-ethylcarbazole, even though the latter has less donor strength. The work of David et al^{95} (1976) appears to increase the evidence in favor of greater reactivity of small model compounds than the corresponding large molecules towards CT complex formation. They reported higher K values for naphthalene and ethylnaphthalene CT complexes with chloranil than for the corresponding complex with polyvinylnaphthalene.

Although the experimental approach involved in the preceding works has the advantage of specificity in interaction (involving only the combination of a donor and an acceptor), its sensitivity is limited by the fact that the weak CT complexes formed, generally do not exhibit any absorption and emission spectra of their own, and only slight shifts of the parent absorption peaks are used to monitor CT interaction.

A second spectrophotometric approach is by fluorescence quenching. The quenching of fluorescence by a foreign substance results from a collision, with formation of a transistory charge transfer complex⁹² between the excited molecule and the quencher. As a result of this bimolecular process, the intensity of fluorescence (I) depends on the concentration (C) of quencher, according to the Stern-Volmer relation,

$$I_{0}/I = 1 + KC$$
 (5.2)

where I_0 is the intensity in the absence of quencher, and K is the Stern-Volmer (quenching) constant. Thus, this approach involves the determination of Stern-Volmer constants, which serve as a measure of the extent of fluorescence quenching by molecular collision. The works of Duportail et al⁹³ (1974) and Tazuke et al⁹⁴ (1975) appear to be the only reported cases of this approach.

Duportail et al, carried out quenching of fluorescence of diphenylanthracene and perylene with the following quenchers: dimethylparatoluidine (DMPT), polymers and copolymers of dimethylaminostyrene. They reported higher quenching constants for DMPT than for the polymers and copolymers, irrespective of the fluorescent molecule. They explained these results in terms of the steric influence of the chain, which limits the possible ways of approach towards the reacting group. Tazuke et al⁹⁴, studied the quenching of fluorescence of the anthryl group of an ester by the anilino group of a series of polyesters and their monomer model compound. Again, higher quenching constant was found for the monomer model compound than for the polymers. They advanced two explanations for this: smaller diffusion constants of polymer quenchers and possible overlap of quenching diameters in the polymers due to congestion in the chain.

However, this approach is not without serious limitations. Deviation from a linear Stern-Volmer plot can arise mostly at high concentrations of either the fluorescent or quenching molecules. In the first case, the deviation is largely due to resonance energy transfer in the polymer. In the second case, it arises from a change of the rate determining step as a function of the concentration of the quencher. Besides, the observance of a linear plot may not always prove that the fluorescence quenching is occurring by a bimolecular collisional mechanism.

The third spectrophotometric approach, utilizes the formation of an exciplex, which we defined in chapter one as an excited state molecular complex, formed between an excited fluorescent moiety and a dissimilar molecular moiety in the ground state. Its formation is accompanied by the quenching of monomer fluorescence. This approach

appears to offer two ways of determining relative reactivity: by exciplex formation and by fluorescence quenching. To our knowledge, the only reported use of this approach, appears to be the work of David et $a1^{95}$ (1976). They studied intermolecular exciplexes, formed by polyvinylnaphthalene, polyacenaphthalene and acenaphthalene, with N,N-diethylaniline (donor) and dicyanoanthracene (acceptor). Plots of the ratio of intensities of exciplex and monomer emissions, $\mathbf{I}_{\mathrm{E}}/\mathbf{I}_{\mathrm{M}},$ versus concentration of quencher, showed greater slopes for the small molecule model compounds than for the corresponding polymers. This indicates greater reactivity of the former compounds towards exciplex formation. However, the use by the authors, of fairly high amounts of the polymers and model compounds as quenchers is likely to have caused substantial differences in medium viscosities between polymer and model compound solutions; and since exciplex formation is a diffusion-controlled process, its rate constant will be proportional to the viscosity of the medium. Thus, the observed lower rate constants for exciplex formation in the polymers might have resulted, partly from the higher viscosities of polymer solutions, and partly from lower frequency factor arising from inaccessibility of reactive sites of the polymer sidechain. The problem of viscosity differences, can however be eliminated, by keeping polymer concentration low and constant, and using varying amounts

of a small molecule as quencher.

In any event, the specificity of an exciplex interaction, which leads to the formation of a transiently stable and fluorescent complex, makes it a potentially reliable technique for studying polymer effect on reactivity. Besides, the interaction is purely physical in nature with no permanent alteration in the electronic and geometric structure of the interacting components.

From the foregoing accounts on some of the early and recent works on polymer effect on reactivity, it can be seen that results are not totally in agreement, though there is greater evidence in favor of small molecules as being more reactive than the corresponding large molecules. Furthermore, only the works of Hayashi and Tazuke³⁶, and Tazuke et al⁹⁴ dealt with the influence of the distance of separation between chromophores in the chain, on their reactivity. While Hayashi and Tazuke found no systematic trend in the equilibrium constants of polymer CT complexes as a function of the distance of separation between the reactive chromophores, Tazuke et al reported smaller Stern-Volmer quenching constants for polymers with congested reactive chromophores.

In this chapter therefore, we will seek further experimental evidence on any differences in the reactivity of a chromophore due to its binding in a polymer chain and separation in a polymer chain with the general objective

of throwing some light on:

the flexibility of randomly coiled polymer chains, and the rate with which such flexible polymer molecules change their shape.

To do this, we will study fluorescence quenching and intermolecular exciplex formation, involving the polyamides: P-2, P-4, P-6, P-8, and the monomer model compound MC, as acceptors, and triethylamine (TEA) as donor (quencher). (See Chapter 4 for structures of the above compounds.)

Exciplexes of P-2, P-4, P-6 and MC with Triethylamine

To dilute solutions (1 x 10^{-4} M/L in CH_2Cl_2 of the polyamides: P-2, P-4, P-6, P-8 and MC, were added increasing amounts of triethylamine (TEA). The fluorescence spectra of these solutions were taken at room temperature in 1 cm square cell. The fluorescence spectra of P-4/TEA solutions are given in Figures 5.1 and 5.2. Similar fluorescence spectra were obtained for solutions of TEA with the other polymers and the monomer model compound.

Figure 5.1 indicates a gradual quenching of the monomer (naphthalene) fluorescence, accompanied by the emergence and growth of exciplex fluorescence (broad band), as the concentration of TEA (donor) is increased.







Monomer and exciplex fluorescence maxima are at 362 and \sim 500 nm respectively. Figure 5.2 shows that, maximum exciplex fluorescence intensity is attained at \sim .09 M/L of TEA, beyond which, quenching of exciplex emission occurs, as well as that of monomer fluorescence; also, past this optimal concentration, the isoemissive point is lost.

Plots of intensity ratios of exciplex and monomer bands, I_E/I_M , as a function of donor concentration, [TEA], are given in Figure 5.3; the slopes of these lines, ξ , are given in Table 5.1. If I_E/I_M ratio is taken as a measure of the extent of exciplex formation, then our results show that the monomer model compound is more reactive than the polymers; and among the polymers, the order of reactivity is as follows: P-8 > P-6 \approx P-4 > P-2. Stern-Volmer plots (Figure 5.4) show deviations from linearity for all the compounds, at high donor concentrations. However, from the initial slopes at low donor concentrations, higher quenching constants, K are obtained for the polymers than for the monomer model compound (Table 5.1). Plots for P-2, P-4 and P-6 show approximately the same initial slopes, with that of P-8 being higher.

Fluorescence decay times, $\tau_{\rm M}$ and $\tau_{\rm E}$ for monomer (in absence of quencher) and exciplex, respectively, were measured by single photon counting technique, and are reported in Table 5.1. Our results show that the decay





Compound	τ _M (nsec)	^k ∭ (10 ⁷ s ^{−1})	^τ E (nsec)	(10 ⁷ s ⁻¹)	К	ξ
MC	19.60	5.10	11.90	8.40	25	14
P-2	19.20	5.20	14.20	7.00	~43	6.60
P-4	19.70	5.10	12.70	7.90	~43	∿8.30
P-6	20.20	5.00	14.20	7.10	~43	∿8.30
P-8	19.80	5.10	13.40	7.50	50	9.60

Table 5.1. Photophysical Parameters for Exciplex Formation.



times for polymer exciplexes with TEA are on the same order of magnitude; however, that of the monomer model compound is slightly lower. Also, decay time (τ_M) of the naphthalene moiety in absence of quencher remains essentially the same in the polymers and the model compound. We will attempt, in the following sections, to explain these results.

Kinetics of Intermolecular Fluorescence Quenching and Exciplex Formation

In donor-acceptor systems, in which exciplex formation can be effected by selective excitation of one of the components, the resulting quenching of monomer fluorescence may not be due to exciplex-formation process alone. Evidence for this, comes from the fluorescent behavior of some composite systems, with donor-acceptor moieties separated by a chain. For example, Davidson and Tretheway⁹⁶ (1976), have shown that monomer fluorescence quenching is more efficient in naphthylbutylamine than in naphthylpropylamine, despite the fact that the latter compound forms a much more stable, and intensely fluorescent exciplex, than the former. Also, in our work, $I_{\rm E}/I_{\rm M}$ ratio continues to increase as a function of quencher concentration, even when the exciplex intensity, I_E has started to decrease. Thus, it appears that in both of the above two cases, monomer fluorescence quenching may involve

the formation of a non-fluorescent excited state complex, in addition to exciplex formation.

Therefore, for a kinetic analysis of the fluorescence quenching and exciplex formation occurring in our systems, we propose the following mechanism:



where A and D represent the acceptor and donor respectively. $(A^{-}D^{+})^{*}$ is the intermolecular exciplex, which we can designate as E^{*}; and $(A^{*}...D)$ is a transitory non-fluorescent CT complex, which we can designate as an encounter complex (EC). In our case, A and D will represent naphthalene and triethylamine moieties respectively. We will therefore refer to the fluorescence of A^{*} as monomer fluorescence. The following rate constants can be defined:

 k_{FM} : fluorescence of monomer k_{IM} : internal quenching of monomer k_{FM} : exciplex formation $\begin{array}{l} {}^{k}{}_{FE} : \mbox{fluorescence of exciplex} \\ {}^{k}{}_{ME} : \mbox{dissociation of exciplex} \\ {}^{k}{}_{IE} : \mbox{internal quenching of exciplex} \\ {}^{k}{}_{1} : \mbox{encounter complex formation} \\ {}^{k}{}_{2} : \mbox{dissociation of encounter complex} \\ {}^{k}{}_{c} : \mbox{thermal de-activation of encounter complex}. \end{array}$

For simplification we also define the following parameters:

$$k_{M} = k_{FM} + k_{IM}$$

$$k_E = k_{FE} + k_{IE}$$

Under steady excitation with light intensity I_a einsteins $l^{-1}s^{-1}$, the rate equations are:

$$\frac{d[A^*]}{dt} = I_a + k_2[EC] + k_{ME}[E^*] - (k_1[D] + k_{EM}[D] + k_M)[A^*]$$
(5.3)

$$\frac{d[E^*]}{dt} = k_{EM}[A^*][D] - (k_{ME} + k_E)[E^*]$$
(5.4)

$$\frac{d[EC]}{dt} = k_1[A^*][D] - (k_2 + k_c)[EC]$$
(5.5)

Assuming photostationary conditions

$$\frac{d[A^*]}{dt} = \frac{d[E^*]}{dt} = \frac{d[EC]}{dt} = 0$$

then

$$[A^*]_{stat} = \frac{I_a}{X - (Y + Z)[D]}$$
(5.6)

and

$$[E^*]_{stat} = \frac{k_{EM}I_a[D]}{(k_{ME}+k_E)[X-(Y+Z)[D]]}$$
(5.7)

where $Y = k_1 k_2 / k_2 + k_c$, $Z = k_{EM} k_{ME} / k_{ME} + k_E$ and $X = [(k_1 + k_{EM})[D] + k_M]$. The intensity of monomer and exciplex fluorescence is given respectively by

$$I_{M} = k_{FM}[A^*]$$
 (5.8)

and

$$I_{E} = k_{FE}[E^{*}]$$
 (5.9)

Putting Equations (5.8) and (5.9) into (5.6) and (5.7) respectively, we get that

$$I_{M} = \frac{k_{FM}I_{a}}{X - (Y + Z)[D]}$$
(5.10)

$$I_{E} = \frac{k_{FE}k_{EM}I_{a}[D]}{(k_{ME}+k_{E})[X-(Y+Z)[D]]}$$
(5.11)

Then

$$\frac{I_{E}}{I_{M}} = \frac{k_{FE}k_{EM}[D]}{k_{FM}(k_{ME}+k_{E})} = \xi[D]$$
(5.12)

From Equation (5.10), we have that

$$\frac{1}{I_{M}} = \frac{X - (Y + Z)[D]}{k_{FM}I_{a}}$$
(5.13)

so that

$$(I_{o}/I)_{M} = \frac{X - (Y + Z)[D]}{k_{FM}}$$
 (5.14)

where I_0 is the monomer fluorescence intensity in absence of donor (quencher)

Equation (5.14) can be simplified to

$$(I_{O}/I_{M}) = 0 + \frac{[k_{1}k_{c}(k_{ME}+k_{E})+k_{EM}k_{E}(k_{2}+k_{c})][D]}{k_{M}(k_{2}+k_{c})(k_{ME}+k_{E})}$$

= 1 + K[D] (5.15)

If we assume that $k_E >> k_{ME}$ and $k_c >> k_2$ then Equation (5.15) reduces to

$$(I_{o}/I)_{M} = 1 + \frac{k_{1}k_{EM}[D]}{k_{M}}$$
 (5.16)

Equation (5.16) is a Stern-Volmer-type relation, but with an additional rate constant, k_1 , to account for quenching of monomer fluorescence due to formation of non-fluorescent CT complex.

Discussion

The relative slopes of the lines in Figure 5.3 may be explained in terms of Equation (5.12). The slope of each line is then equal to $k_{FE}k_{EM}/k_{FM}(k_{ME}+k_E)$. Since the plots are within the optimum donor concentration for exciplex formation, we can assume that $k_E >> k_{ME}$; and since k_{FM} does not vary significantly among the polymers and the model compound (Table 5.1) it is seen that k_{EM} , (the rate constant for exciplex formation), is larger for the model compound than for the polymers. This greater reactivity of the monomer model compound towards intermolecular exciplex formation may be attributed to two main factors:

First, since exciplex formation is a diffusion-controlled process, we may approximate $k_{\rm EM}$, the rate constant for exciplex formation, by⁹⁴

$$k_{\rm EM} \sim 4\pi \rm ND(\gamma R_{o}) \cdot 10^{3}$$

where γR_0 is the effective action diameter, D is the sum of diffusion constants for acceptor and donor molecules, and N is avogadros number.

The slow motion of polymer molecules would lead to comparatively much lower D values. Second, the steric strain of the polymer chain would restrict the ability of the naphthalene moiety to assume the optimum configuration for effective exciplex interaction. The model compound,

on the other hand, is free to rotate and translate, and thus can readily attain with donor molecules, the optimum configuration necessary for exciplex formation.

Among the polymers, we noted that the order of reactivity is P-8 > P-6 \approx P-4 > P-2. It appears that reactivity increases with increase in the length of the methylene-chain in the polymer backbone. Increase in methylenechain length means increase in chain flexibility; consequently, steric restrictions on the motion of chain naphthalene moieties will decrease in the order: P-2 > P-4 > P-6 > P-8; leading to the order of reactivity stated above, and depicted in Figure 5.5.

The indication from the initial slopes of the Stern-Volmer plots (Figure 5.4) that the quenching constant (K) for the model compound is smaller than those for the polymers, appears anomalous, on the basis of our earlier argument that the model compound possesses a much larger diffusion constant than the polymers. However, from our kinetic analysis of some of the physical processes involved in monomer fluorescence quenching and exciplex formation, one can see from Equation (5.15), that the quenching constant, K, is a complex term, involving many rate constants. And without knowing the values of k_{ME} , k_1 and k_2 , it is hard to assess the contributions of the diffusion-dependent rate constants, such as k_{FM} .

The observed deviations from linear Stern-Volmer plots





at high donor concentrations seems to indicate a change in the rate determining step for monomer fluorescence quenching. The rate of collision of reactants may have ceased to be the rate determining step; instead a state of equilibrium may exist between donor and acceptor molecules, leading to the formation of non-fluorescent CT complexes; so that K may in fact be the equilibrium constant for the CT complex. If that is the case, the greater stability of the CT complexes with the polymer versus that with the model compound may be due to a lesser degree of dissociation in the case of the polymer.

Thus, in conclusion, it seems that <u>use of monomer</u> <u>fluorescence quenching as a measure of reactivity is not</u> <u>dependable, when more than one process is involved in the</u> <u>quenching</u>. On the other hand, <u>intermolecular exciplex</u> <u>formation appears to be an effective method for establish-</u> <u>ing the extent to which the physical reactivity of a chemi-</u> <u>cal moiety can be affected as a result of binding in a</u> <u>polymer chain</u>. Also, intermolecular exciplex interaction involving a chain-bound reactive group appears sensitive to the flexibility of the intervening chain.

CHAPTER 6

SOLVENT-INDUCED INTRAMOLECULAR EXCIPLEX FLUORESCENCE IN 2,6-BIS(METHYLAMINO)NAPHTHALENES

Introduction

Studies on intramolecular exciplex formation have focused on two main issues: the geometric requirements and the role of the solvent.

In our consideration of intramolecular excimer formation (Chapter 4) we saw that the observance of excimer fluorescence is dependent upon the length and chemical constitution of the intervening chain, and upon the chemical nature of the chromophore. Excimer interaction, because it arises predominantly from exciton resonance, is maximized when the interacting chromophores are in a sandwich configuration; the attainment of this configuration as we saw, is optimized when the chain between the interacting groups consists of three atoms. Thus, the spectral position of excimer emission depends only on the free energy of formation, and the ground state repulsion, being generally insensitive to external parameters, such as the polarity of the medium. This is largely due to the fact that the dipole moment of the excimer state is essentially zero.

However, the charge transfer (CT) character of the

exciplex state (with a net dipole moment) makes it highly susceptible to solvation. Thus, the energies, fluorescence intensities and decay times of exciplexes are known to decrease with increase in solvent polarity.²¹⁻²³

The additional stabilization of the exciplex state via solvation has led to the observance of intramolecular exciplex fluorescence in polar media, under stringent geometric conditions: Chandross and Thomas (1971)²⁴, studied naphthyl(CH2), amine system, in hydrocarbon solvents, and observed exciplex emission only in n=2-4. However, recent reports by Davidson, et al^{96} and Ibemesi, et al^{73} show that naphthylmethyl amines (n=1), exhibit solventinduced intramolecular exciplex emission. A number of studies, 97-100 have shown the same solvent effects on intramolecular exciplex emission in the system $p-(CH_3)_2NC_6H_4 (CH_2)_n$ (9-anthryl or 1-pyrenyl), in which only fluorescence emissions typical of 9-ethylanthracene (n=l and 2) and 1-ethyl pyrene (n=1) are observed. However, in ether solutions, exciplex fluorescence is observed, in addition to the fluorescence of the excited aromatic chromophore. In the aromatic hydrocarbon-aromatic amine systems, the non observance of exciplex emission in hydrocarbon solvents is not accompanied by quenching of monomer fluorescence.

However, in aromatic hydrocarbon-aliphatic amine systems, there is considerable quenching of aromatic (monomer) fluorescence in hydrocarbon solvents, even though

exciplex emission is not detectable. Sufficient experimental evidence is lacking on the mechanism of this quenching. The author and coworkers⁷³ have recently proposed the involvement of a charge transfer state, which may mix with the locally excited singlet states, resulting in spinorbit coupling. This would make intersystem crossing competitive with monomer fluorescence. Such proposition was based on the observed decrease in the phosphorescence lifetime and enhancement of phosphorescence yield in β -naphthylmethylamine (β -NMA) relative to β -methylnaphthalene (B-MN). Earlier, McGlynn and co-workers¹²⁰ had demonstrated that charge transfer (CT) states resulting from intermolecular interaction in donor-acceptor systems produce a decrease in the phosphorescence lifetime of the donor molecule and an increase in the phosphorescence-fluorescence quantum yield ratio , ϕ_p/ϕ_F . Also, Toumon and El-Bayoumi¹²¹ (1972) made similar observations in benzyl derivatives (such as benzylamine and benzyl alcohol), which showed an enhancement of phosphorescence yields, a quenching of fluorescence intensities and a shortening in their natural phosphorescence lifetime, τ_p^o , relative to toluene. Goldschmidt et al¹²² have shown by flash photolysis, the formation of triplet states in the charge-transfer quenching of fluorescence of aromatic molecules.

The study of the fluorescence properties of 2,6-bis (methylamino) naphthalenes, II-IV, which are disubstituted

symmetric analogs of β -NMA, is thus undertaken to provide further experimental evidence for fluorescence quenching via a CT-induced intersystem crossing. Also the effect of N-methylation on the fluorescence properties of these amines will help to expose more clearly the involvement of the lone pair on the nitrogen in both the quenching of monomer fluorescence and the formation of fluorescent intramolecular exciplex, under stringent geometric conditions.



2,6-Bis(methylamino)naphthalenes (II-IV)

Absorption and Emission Properties of 2,6-Bis(methylamino) Naphthalenes, II-IV.

Room temperature absorption spectra of dilute solutions $(1 \times 10^{-4} \text{ M/L})$ of compounds I-IV in ethanol, are given in Figure 6.1. The absorption bands appear very similar, except there is substantial blurring of the long wavelength $({}^{1}L_{b})$ bands (\sim 322-300 nm) in compounds II-IV, being most pronounced in compound IV. Also, the intense ${}^{1}L_{a}$ transition





band $(\lambda_{ab}^{\max} \sim 272 \text{ nm})$ appears less resolved in compounds II-IV. A molar extinction coefficient of ~ 5000 (at 290 nm) is obtained for all four compounds in ethanol. The absorption spectrum of IV in a number of solvents of different polarities are identical, with a select few displayed in Figure 6.2. However, there is slightly more blurring of the ${}^{1}L_{b}$ bands in methanol, while the ${}^{1}L_{a}$ band is slightly better resolved in the same solvent.

Room temperature fluorescence spectra of dilute solutions (l x 10^{-4} M/L) of compounds I-IV in ethanol, are shown in Figure 6.3. Compound I, as expected, gives only the monomer (naphthalene) fluorescence. However, significant differences are evident in the fluorescence spectra of compounds II-IV:

i) Monomer fluorescence quenching occurs in all three
compounds to different degrees, in the order, IV > III >
II.

ii) A broad structureless band, due to an intramolecular exciplex, is present, the intensity of which, increases in the order, IV > III > II. Consequently, the ratio of intensities of exciplex to monomer emissions, I_E/I_M , is highest in IV, followed by III, and least in II (Table 6.1).

iii) The exciplex emission maxima in the three compounds, occur at different energies, in the order II > III > IV, (Table 6.1).

iv) The emission spectra of II, III and IV, taken in







Figure 6.3. Enhancement of intra-molecular exciplex emission on N-methylation: —— Cpd I, ... Cpd II, ---- Cpd III, ---- Cpd IV. λ_{ex} 290 nm, solvent: ethyl alcohol.

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Quant1ty	Solvent	Temperature	г	II	III	IV
λ ^{max} (rm)	Ethanol	25°C	8 8 9	450	469	491
$I_{\rm E}/I_{\rm M}$	Ethanol	25°C	1 1 1 1	0.05	0.55	3.60
ХФ Д	3-Mepentane	25°C	0.300	0.138	0.123	0.061
τ _F (nsec)	3-Mepentane	25°C	36.60	22.60	20.90	4.10
I_p/I_F	3-Mepentane	77K	10.0	0.14	0.16	0.17
τ _p (sec)	3-Mepentane	77K	0.32	0.32	0.32	0.39
τ _p (sec)	Ethanol	77K	0.35	1.41	2.67	3.16
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other solvents of high polarities ($\varepsilon > \sqrt{15}$) show the same trends observed in ethanol.

v) In moderately polar solvents ($\varepsilon < 10$), only exciplex fluorescence is observed in IV; while in III, it appears as a shoulder, and virtually non-existent in II. Since compound IV, gives the most intense exciplex emission, its fluorescence spectra in solvents of different polarities are given in Figure 6.4. Exciplex fluorescence maxima (λ_E^{max}) and quantum yields (Φ_E) in these solvents, are given in Table 6.2. The following trends are observed as solvent polarity (dielectric constant) increases:

i) Exciplex emission maxima shifts to longer wavelength.

ii) Exciplex fluorescence quantum yield is relatively higher in moderately polar solvents ($\varepsilon < 10$) than in highly polar solvents ($\varepsilon > \sim 15$). However, there is a reverse trend in $\Phi_{\rm E}$ from methanol ($\varepsilon = 32.70$) to acetonitrile ($\varepsilon = 38.8$) (Figure 6.5).

A plot of exciplex emission maximum versus solvent polarity parameter is made (Figure 6.6) using Equation (2.53), given below.

$$hv_E = hv_0 - \frac{\mu_e^2}{a^3} \left[\frac{2(\epsilon-1)}{(2\epsilon+1)} - \frac{n^2-1}{2n^2+1}\right]$$

A dipole moment of 14.4D is calculated for the exciplex, assuming a cavity radius of 4.8 Å.



Figure 6.4. Fluorescence spectra of compound IV in solvents of different polarities. 1) 3 Me-Pentane, 2) Iso-propyl alcohol, 3) methanol, 4) methylene chloride.
Solvent	Dielectric Constant	λ ^{max} M (nm)	λ ^{max} E (nm)	$\Phi_{\rm E}$
3-Mepentane	2.020	346		
Dioxane	2.209		458	0.020
Diethyl ether	4.235		429	0.015
Methylene chloride	8.93		455	0.017
1-Butanol	17.51	339	480	0.011
Ethyl alcohol	24.55	343	491	0.007
Methyl alcohol	32.70	339	498	0.004
Acetonitrile	38.80		∿500	0.010

Table	6.2.	Exciplex	Fluor	esce	nce	Quantum	Yields	and	Emis-
		sion Max	ima in	IV	in I	Different	Solver	nts.	



Exciplex fluorescence quantum yield, ϕ_E , as a function of solvent dielectric constant, $\varepsilon.$ Figure 6.5.



Figure 6.6. Determination of dipole moment of exciplex (IV).

From Figure 6.4, it can be seen that compound IV does not give exciplex emission in 3-methyl pentane (a hydrocarbon solvent), compound II and III behave similarly. Monomer fluorescence quantum yield (Φ_F^M) and decay time (τ_F^M) of II-IV in 3-methylpentane are given in Table 6.1. Values of Φ_F^M and τ_F^M increase in the order II > III > IV.

Total emission measurements were carried out at 77 K, in 3-methylpentane; the observed fluorescence and phosphorescence spectra are shown in Figure 6.7. Compound I shows extremely weak phosphorescence component; while the total emission spectra of compounds II and III seem to indicate the presence of a third peak, lying between the monomer fluorescence and phosphorescence. Compound IV, on the other hand, shows only monomer fluorescence and phosphorescence bands, which are well-resolved. Ratios of intensities of monomer phosphorescence to monomer fluorescence, I_p/I_F , for all four compounds are given in Table 6.1 with magnitudes in the order IV > III > II > I. Phosphorescence life times determined in 3-methylpentane are in the order: IV > III = II = I (Table 6.1).

Similar total emission measurements were done in ethanol. The following observations are made:

i) Monomer fluorescence is absent in IV, weak in III, relatively intense in II and very intense in I.

ii) Monomer phosphorescence increases in intensity,in the order, IV > III > II > I. Accurate intensity ratios



of monomer fluorescence and monomer phosphorescence could not be taken because of the weak intensity of either one or the other of the components.

iii) Results of monomer phosphorescence lifetime measurements in ethanol (Table 6.1) show the following increasing order: IV > III > II > I.

Exciplex fluorescence life times of compounds II-IV in polar solvents, were too short (<2 nsec) to be determined by our single photon counting instrument, which has a pulse width of \sim 2 nsec.

Discussion

The blurring of the ${}^{l}L_{b}$ absorption bands, and the less resolved nature of the ${}^{l}L_{a}$ band in compounds II-IV, compared to compound I, appears to indicate some ground state charge transfer (CT) interaction between the aromatic group and the amino group, despite the intervening methylene group. These bands become resolved on addition of acid or water (Figure 6.8), which tends to support the above suggestion. Protonation and/or strong hydrogen-bonding with water would destroy the donating ability of the nitrogen lone pair.

However, N-methylation does not lead to any detectable differences in the absorption spectra of compounds II, III and IV, either in polar or non-polar media. Thus, the



Figure 6.8. Room temperature absorption spectra: 1) I, 2) III, 3) III + 90% H₂O, 4) III + 1 drop of CF_3COOH . λ_{ex} 290 nm.

observed differences in their emission spectra reflect differences in their excited state properties and not ground state interactions.

The enhanced exciplex intensity on N-methylation seems to arise from the decrease in ionization potential of the amines. If we approximate the exciplex energy, $E(A^{-}D^{+})$, by Equation 2.23, given below:

$$E(A^{-}D^{+}) = IP_{D} - EA_{A} - C$$

then compound IV with the least ionization potential, will form the most stable exciplex, since the other energy terms $(EA_A \text{ and } C)$ are essentially the same for the complexes of the three compounds. Thus the increase in exciplex fluorescence intensity on N-methylation clearly demonstrates the involvement of the nitrogen lone pair in exciplex formation. A further confirmation of this is given by the observed total quenching of exciplex emission, on protonation of the amino group.

The observance of exciplex emission only in moderate to highly polar solvents could be explained as follows: Because of the asymmetric location of the donating orbital of the amino group with respect to the accepting orbital of the aromatic group, the stabilization energy of the CT state due to coulombic forces may be small. However, since the dipole moment in the CT state is large (14.4D for IV),

solvation in a polar solvent, may be very effective for the stabilization of the CT state. Increase in solvent polarity will increase the amount of stabilization by solvation; so that exciplex energy will be correspondingly lowered, hence the observed spectral shifts.

It appears that the dipolar character of the exciplex of IV (μ = 14.4D) is very similar to that of β -naphthylmethylamine, β -NMA (μ = 14.6). The use of Equation (2.53) in determining absolute dipole moments for these complexes, is subject to error due to the following assumptions or approximations:¹⁰¹

i) The radius of the solvent cage (a) surrounding the complex is only an estimate, which could be in error by as much as 20%.

ii) Equation 2.53 is derived on the assumption that
the electronic structure of the exciplex does not change on
solvation; however, solvent-exciplex interaction can occur
and will induce changes in the geometry of the complex.
Such specific interactions will cause scatter in plots of
the above equation, as may be evident in Figure 6.6.

However, if $\overline{\nu}_{\rm E}^{\rm max}$ values for two different complexes are plotted against each other, the solvent-solute interactions largely cancel, and yield relative values of $\mu^2/h_{\rm c}a^3$, which may be compared. This is shown in Figure 6.9 for compounds IV and β -NMA. A slope of one is obtained, showing that μ^2/hca^3 (IV) = μ^2/hca^3 (β -NMA); which seems to validate



Figure 6.9. Plot of maximum of exciplex emission for IV against maximum of exciplex emission for β -NMA.

the absolute values obtained for their dipole moments.

The decrease in exciplex fluorescence quantum yield at high solvent polarities (Figure 6.5) may be due to formation of non-fluorescent solvated ion pairs from the encounter complex (with rate constant k_q) and from the exciplex (with rate constant k_T).



According to this mechanism, 102 illustrated above, k_q and k_I are assumed to increase with increase in solvent polarity. The exciplex quantum yield will be proportional to $k_{EM}/k_{EM} + k_q$. In intermolecular exciplexes, ion radical formation has been reported in many Laser photolysis studies, $^{21},^{22},^{103-107}$ in which absorptions corresponding to the ionic dissociation products A_s^- and D_s^+ have been detected. It has also been shown that the dissociation into ions occurs from the non-relaxed CT system (encounter complex) before the relaxed exciplex state is formed.¹⁰⁸ However, such ion radical formation is unlikely in intramolecular exciplexes; this probably accounts for the fact that the latter generally exhibit higher fluorescence quantum yields in polar media than their intermolecular counterpart. For example, the intramolecular exciplex of compound IV has a quantum yield of 0.004 in methanol, but the intermolecular exciplex of naphthalene and triethylamine is not observed in the same solvent.¹⁰⁹

The initial increase in exciplex quantum yield (Figure 6.5) in moderately polar media seems to reflect the solventinduced nature of exciplex fluorescence in these amines; thus indicating that a certain solvent polarity is necessary for optimum exciplex stability.

The relatively lower quantum yields observed in ethyl alcohol and methyl alcohol, compared to acetonitrile, seem to indicate an effect arising from some solvent property other than polarity. For example, specific interaction between the hydroxylic solvent molecules and the amino group could reduce the reactivity of the lone pair in CT interaction, with the excited singlet aromatic group. There is also the possibility of quenching of the exciplex fluorescence by specific interaction of the exciplex with hydroxylic solvent molecules.

The high quantum yield of exciplex fluorescence in dioxane, despite its low dielectric constant, again suggests

some form of specific interaction between solvent molecules and the exciplex; the high electron density on dioxane oxygens could exert some stabilizing effect on the exciplex, due to the CT character of the latter. A detailed study of the specificity of exciplex interaction with polar molecules is undertaken in the next chapter.

On the whole, exciplex fluorescence quantum yields in IV are quite low, and with very short life time (which could not be measured by our single photon counting setup); all this indicates that intramolecular exciplex formation in IV as well as in II and III, is very inefficient, due to geometric restrictions imposed by tetrahedral bond angles. The overlap of the nitrogen lone pair orbital with the π -orbital of the ring is very poor.

The observation that monomer fluorescence quenching in a hydrocarbon solvent increases in the order IV > III > II (which is the same order of increase in exciplex intensity in polar solvents) appears to suggest the involvement of the same molecular intermediate in both monomer fluorescence quenching and exciplex formation. This intermediate is probably an encounter complex, with a partial charge transfer character, and an energy that lies close to that of the locally excited single state. In a hydrocarbon medium, the encounter complex is relatively high in energy due to lack of stabilization by solvation; but it may mix with the locally excited singlet state, leading to enhanced

spin-orbit coupling. The latter, in turn, leads to an increase in intersystem crossing to the triplet state - process 2 in the scheme below.⁷³

At room temperature, the resulting excited triplet state will however undergo thermal dissociation. But at 77 K



(liquid N₂ temperature), if intersystem crossing (process 2) is competitive with monomer fluorescence (process 4), then from Equations (6.1 to 6.3),¹¹⁰ one would expect to observe an increase in the phosphorescence/fluorescence ratio, Φ_p/Φ_F .

$$\Phi_{\rm p}/\Phi_{\rm F} = k_{\rm p}\tau_{\rm p}(\frac{1}{\Phi_{\rm F}} - 1)$$
 (6.1)

$$\tau_{\rm p} = 1/k_{\rm p} + k_{\rm m} \tag{6.2}$$

$$\Phi_{\rm F} = k_{\rm F}/k_{\rm F} + k_{\rm n} + k_{\rm g}$$
 (6.3)

where

- $\tau_{\rm p}$ = observed phosphorescence lifetime
- $k_{\rm p}$ = rate constant for phosphorescence
- k_m = rate constant for thermal deactivation

of excited triplet state

- k_g = rate constant for intersystem crossing
- k_F = rate constant for fluorescence
- k_n = rate constant for internal conversion of first
 excited singlet state.

Total emission measurements at 77 K, carried out with compounds I-IV in 3-methylpentane, show that Φ_p/Φ_F , has increased in II, III and IV by a factor of 14, 16 and 17 respectively, relative to I. From Equation (6.3), it is clear that the observed decrease in monomer fluorescence quantum yield at 77 K, must be due to an increase in k_g , since k_n will in fact be negligibly low. Similar phosphorescence enhancement is observed in ethanol, with compound IV exhibiting only phosphorescence emission; indicating that intersystem crossing is predominant in depopulating the excited singlet state. Some degree of stabilization of the transient CT state by the frozen polar solvent molecules may lead to greater mixing with locally excited state.

The observed increase in phosphorescence life times, for example, in IV compared to I, appears contrary to expectation; because enhancement of intersystem crossing will lead to an increase in k_p , and hence a decrease in τ_p . However, from Equation (6.2), it is possible that the increase in k_p may have been offset by a decrease in k_M .

Viscosity Dependence of Exciplex Emission in III and IV

The fluorescence emission bands of compounds III and IV are similarly affected by the viscosity of the medium. The case of IV is shown in Figure 6.10. The following observations are made for both compounds:

i) There is a gradual quenching of exciplex fluorescence, with corresponding increase in monomer fluorescence, as viscosity of the medium increases. However, the exciplex emission is not completely quenched even in 100% glycerol.

ii) As the glycerol content is increased, there is a slight shift to the red in exciplex emission maxima by 6.5 nm in III and $\sim 4.5 \text{ nm}$ in IV.

iii) A plot of the ratio of intensities of monomer and exciplex fluorescence, I_M/I_E against viscosity of the



Figure 6.10. Effect of viscosity on fluorescence spectra of compound IV. Solvent: Ethanol/glycerol mixture. % Glycerol: 1) 0, 2) 5, 3) 40, 4) 80; λ_{ex} 290 nm.

medium (Figure 6.11) is linear in the high viscosity region $(n \ge 30 \text{ cp})$, but curved towards the abscissa at low viscosities, making a finite intercept.

The above results can be *r*ationalized, using the same kinetic expression (Equation 4.13) obtained for the case of intramolecular excimer formation.

$$I_{M}/I_{E} = \frac{k_{FM}(k_{E}+k_{ME})}{k_{FE}\cdot k_{EM}}$$

where

$$k_E = k_{FE} + k_{IE}$$

 $I_{M} = \text{monomer fluorescence intensity}$ $I_{E} = \text{exciplex fluorescence intensity}$ $k_{FM} = \text{rate constant for monomer fluorescence}$ $k_{EM} = \text{rate constant for exciplex formation}$ $k_{FE} = \text{rate constant for exciplex fluorescence}$ $k_{ME} = \text{rate constant for exciplex dissociation}$ $k_{TE} = \text{internal quenching of exciplex.}$

The viscosity dependent terms are k_{ME} , and k_{EM} , and if $k_E >> k_{ME}$, then I_M/I_E should be proportional to k_{EM}^{-1} . But k_{EM} is the rate constant for the conformational change involved in exciplex formation, so that I_M/I_E should be linearly related to the viscosity of the medium.

The observance of a linear plot at high viscosities seems to conform to the above kinetic analysis. Although,



Plot of monomer/excimer intensity, I_M/I_E , ratio versus viscosity of medium. Compound IV in ethanol/glycerol mixture. Figure 6.11.

considerable conformational transitions may not be required to attain the exciplex configuration in these naphthylmethyl amines, some rotation about the $C_{al}-C_{ar}$ bond may be necessary to bring the lone pair orbital into closer proximity with the ring orbital; such a rotational transition will be viscosity dependent. The non-linearity in the plot at moderate to low viscosities seems to indicate a more complex dependence, in which the assumption $k_E >> k_{ME}$ may not be valid. The observance of a finite intercept on I_M/I_E axis reflects some degree of insensivity of intramolecular exciplex formation in these amines to low macroscopic viscosities.

The slight shift in exciplex emission maximum may be due to some change in dielectric constant of the medium at high glycerol content. It is also possible that some of the quenching of the exciplex emission may arise from both polarity effect and specific interaction with the hydroxyl groups of glycerol.

Quenching of Exciplex Fluorescence in II-IV by Water

Quenching of intramolecular exciplex fluorescence in compounds II, III and IV is carried out with the following objectives:

1) To dramatize the effect of hydroxylic solvents on exciplex emission, with a view to revealing the specificity of the interaction of such solvent molecules with exciplexes.

2) To examine the relative basicity of N-methylated amines, and hence the electronic and geometric effects of N-methylation, by a bimolecular fluorescence quenching.

The absorption spectrum of dilute solution $(1 \times 10^{-4} M/L)$ of III plus 90% water by volume, is given in Figure 6.8. As noted earlier, addition of water leads to the resolution of both the ${}^{1}L_{b}$ and ${}^{1}L_{a}$ bands; which suggests that some specific ground state interaction occurs between the water molecules and the amine molecules. Compounds II and IV behave similarly.

Exciplex fluorescence in IV, in the presence of varying amounts of water, is shown in Figure 6.12. In IV, as well as in III and II, exciplex emission is gradually quenched with increasing amounts of water; on the other hand, monomer (naphthalene) fluorescence is enhanced. Quenching of exciplex fluorescence is complete on addition of 45% H₂O in III and 85% H₂O in IV; in II, there is residual exciplex band above 85% H₂O.

Plots of the ratio of exciplex fluorescence intensity in absence (I_E°) and presence (I_E) of water, as a function of concentration of water, are given in Figure 6.13. The following Stern-Volmer quenching constants (mole⁻¹ litre) are obtained: 0.068 (II), 0.330 (III) and 0.209 (IV). Also, plots of ratio of monomer fluorescence intensity in presence (I_M) and absence (I_M°) of water, as a function



Figure 6.12. Effect of water on fluorescence emission of compound IV. % H_2O (volume): 1) 0, 2) 5, 3) 15, 4) 50, 5) 85. λ_{ex} 290 nm, solvent: ethanol.





of concentration of water are given in Figure 6.14 (IV) and Figure 6.15 (III).

Quenching of exciplex fluorescence in compounds II-IV, by water, may proceed by two mechanistic path ways, represented in the scheme below:



1) Static Quenching.

This will involve the formation of a complex (AQ) between a ground state molecule (A) of the amine, and a water molecule (Q). This complex, on excitation, can no longer form an intramolecular exciplex, because the lone pair on the nitrogen is bound to water molecule; this will lead to a decrease in exciplex fluorescence intensity, and the observance of a Stern-Volmer relationship. However, the quenching constant will represent the equilibrium



Figure 6.14. Water-induced enhancement of monomer emission in IV. Plot of I_M/I_M° versus % H_2° (volume) in ethanol.



Figure 6.15. Water-induced enhancement of monomer emission in III. Plot of I_M/I_M° versus % H₂O (volume) in ethanol.

constant for the complex formation between A and Q. The excited complex (A^*Q) will emit monomer fluorescence; so that a decrease in exciplex fluorescence intensity will be accompanied by an increase in monomer fluorescence intensity. Also, exciplex fluorescence decay time will be unaffected.

2) Dynamic Quenching

This will proceed by a bimolecular collisional mechanism, involving an exciplex moiety (E) and a water molecule (Q), to form a transient CT complex (EQ)*, which undergoes thermal dissociation to the ground state. The quenching will follow a Stern-Volmer relationship; exciplex fluorescence life time will decrease, and monomer fluorescence will not be enhanced.

The two mechanisms may contribute to the observed quenching of exciplex fluorescence by water. However, static quenching (1), appears predominant at high concentrations of water (> $\sim 20\%$). This is supported by the observed rise in monomer fluorescence. Below 20% of water, the quenching appears to proceed more by dynamic quenching (particularly in III), as evidenced by the constant value of monomer fluorescence intensity.

The basicity of aliphatic amines follows the order: secondary > tertiary > primary. According to this, compound III is the most basic, followed by IV and then II.

The Stern-Volmer quenching constants observed for these compounds follow the order of their basicity. This seems to support the predominance of static quenching of exciplex fluorescence by water. Further evidence for this comes from the effect of water on the absorption spectra of these compounds. Addition of equal amounts of water (50%) to their solutions in ethanol intensified the ${}^{1}L_{a}$ absorption band in the order: III > IV > II. Also the observed resolution of the ${}^{1}L_{b}$ bands correspond to the above order. The lack of significant spectral shift of the exciplex band on addition of large amounts of water (with increase in dielectric constant of the medium) lends support to the smaller role of dynamic quenching. Exciplexes undergo spectral shifts to the red, with increase in dielectric constant of the medium.

Consequently, the observed quenching constants may represent the equilibrium constants for proton exchange between water molecules and ground state amine molecules; in which case the relative basicity of these amines appears to have been established by exciplex fluorescence quenching.

Conclusion

The fluorescent behavior of naphthyl{CH₂}NRR' system (II, III and IV) reported in this chapter have provided further experimental support to the recent findings that

intramolecular fluorescent exciplexes can be formed under stringent geometric conditions (n=1), in polar solvents, due to increased stabilization by solvation. Effects of N-methylation in these amines have helped to demonstrate the involvement of the nitrogen lone pair in both intramolecular exciplex formation in polar solvents, and quenching of monomer fluorescence in hydrocarbon solvents. The latter is shown to proceed via a charge-transfer-induced intersystem crossing enhancement. Quenching of exciplex fluorescence by water appears to typify the specificity of interaction of exciplexes with hydroxylic solvents, and probably other polar solvents. The latter will be reported in the next chapter.

CHAPTER 7

INTERACTION OF AMINE-HYDROCARBON EXCIPLEXES WITH POLAR MOLECULES

Introduction

The fluorescence energies, intensities and decay times of exciplexes are known to decrease with increase in solvent polarities.²¹⁻²³ The decrease in intensity and life time has been attributed to the formation of solvated ion pairs, and/or dissociated radical ions. The red shift in the exciplex emission band with increasing solvent polarity is generally rationalized on the basis of Born solvation of the exciplex. Thus the exciplex energy in solution (Equation 2.53) is believed to depend on solvent polarity parameters - bulk dielectric constant and refractive index. The derivation of the above energy expression is based on Onsanger's continuum model, which envisages the exciplex at the center of a cavity surrounded by a dielectric continuum.

This model excludes the possibility of any specific interaction between the exciplex and polar solvent molecules. However, since exciplexes are highly dipolar in character, with dipole moments in the range of 10-30D, it is therefore, highly probable, that in some polar

media, solvent molecules closest to the exciplex moiety, can interact with it in a specific manner, involving dipole-dipole and dipole-induced dipole forces and/or hydrogenbonding (for protic polar molecules). Generally, the occurrence of such specific interactions are said to lead to scatter in the plot of exciplex emission maximum as a function of polarity parameters (Equation 2.53).

However, E. A. Chandross, and others tend to attribute the red-shift of exciplex emission band with increasing solvent polarity, mainly to specific interaction of the exciplex with individual solvent molecules, rather than to a <u>bulk</u> dielectric continuum. Their contention is based on the experimental observation that addition of small amounts of polar solutes to a hydrocarbon solution of an exciplexforming composite system, causes: a decrease in exciplex fluorescence intensity and a red-shift in exciplex spectral position and a change in exciplex emission band shape.

For example, Chandross and Thomas¹¹¹ (1971), studied the interaction of intramolecular exciplex of naphthylpropyl amine (in benzene) with polar molecules such as propionitrile ($\varepsilon = 27$), hexamethylphosphoramide, HMPA ($\varepsilon = 30$) and dimethyl formamide, DMF ($\varepsilon = 37$). Analysis of the observed quenching of the exciplex fluorescence gave a linear Stern-Volmer relationship at low concentrations of added polar solute. This was believed to be indicative of a 1:1 interaction of the exciplex with a polar molecule.

Also HMPA was found to possess a much higher quenching constant than propionitrile despite the closeness of their dielectric constant. The latter result was attributed to the greater solvating power of HMPA towards a cation. Furthermore, the observance of a change in band shape of the exciplex emission, though at fairly high concentrations of the added polar species (e.g., 5.67 M for HMPA) led Chandross and Thomas to suggest the presence of a new emitting species resulting from a 1:1 interaction between the exciplex and a polar molecule.

However, Selinger and McDonald¹¹² (1971), argued that Chandross's observations are merely due to a change in the dielectric constant of the non-polar solvent as a result of addition of polar molecules. In other words, that the quenching and shift in exciplex emission maximum will not occur if the dielectric constant of the medium remains constant on addition of the polar species. To prove this point, they (Selinger and McDonald) examined the effect of excess diethylaniline on the intermolecular exciplex of anthracene and diethylaniline in cyclohexane and ethylacetate as solvents. Exciplex fluorescence quenching was reported in the former solvent, but not in the latter, in which the dielectric constant of the medium was kept constant. However, the validity of the observation in ethylacetate was challenged by Chandross,¹¹³ who pointed out that ethylacetate, being a moderately lewis-basic

solvent, may have overwhelmed the added polar species by virtue of its much higher concentration; in which case, "levelling effect" appears to account for the non-observance of exciplex fluorescence quenching in ethylacetate.

To buttress his earlier suggestion that dipolar excited states (e.g., exciplexes) do interact in a specific manner with surrounding dipolar species, Chandross¹¹³ studied the fluorescence properties of 9-(4-dimethylaminophenyl)anthracene (for brevity, anilinoanthracene) in methylcyclohexane and toluene. This compound, in the above solvents, shows a fluorescence band typical of 9-phenylanthracene. However, upon addition of small amounts of N,Ndimethyl formamide (DMF) or 0-dichlorobenzene (DCB), the fluorescence spectrum was shifted to the red. The following differences were observed:

i) in methylcyclohexane, adding different amounts of DMF ($\varepsilon = 37$) and DCB ($\varepsilon = 9.9$) to give the same bulk dielectric constant, showed DMF to cause a much larger redshift, and also a more pronounced change in the fluorescence band shape.

ii) adding the same amount of DMF to the solutions of anilinoanthracene in methylcyclohexane and toluene, to give different bulk dielectric constant, a larger redshift of the fluorescence spectrum was found in methylcyclohexane than in toluene, despite the lower bulk dielectric constant of the solution in the former solvent.

The first observation is believed to be due to a weaker interaction of the exciplex with DCB. In the second observation, toluene appears to exert a levelling effect, competing more effectively with DMF in solvating the excited molecule than does methylcyclohexane; however, the observed larger red-shift in a solution with a lower bulk dielectric constant appears to reflect some specific interaction between the excited molecule and DMF.

Although Chandross's results seem convincing in showing that the observed red-shift in exciplex band in the presence of small amounts of polar molecules may be due to some specific interaction, the accompanying decrease in exciplex fluorescence intensity is not explicable on the basis of formation of a new emitting species, believed to arise from a 1:1 interaction of the exciplex with a polar molecule. Dissociation to ions is unlikely to be caused by one polar molecule when the surrounding medium is aliphatic hydrocarbon. Besides, the reported change in exciplex band shape occurs at fairly high concentrations of added polar molecule (>1 M); in this region, effects due to bulk dielectric constant may not be completely ignored. Also, the failure to detect isoemissive points in the emission spectra of most of the studied exciplex-polar molecule interactions, appears to weaken the claim for a new complex formation.

Recently, Beddard et al¹¹⁴ reported the quenching of monomer and intramolecular exciplex fluorescence in

1-(2-naphthyl)-l-hydroxy-3-(N-piperidinyl)-propane (I) on addition of small amounts of ethanol and acetonitrile to a solution of (I) in cyclohexane. A red-shift was observed in both the steady state and time-resolved emission bands of the exciplex. Values for the various excited state rate constants (including that for a 1:1 exciplexpolar molecule complex formation) were obtained. Thus. the suggestion was made for a one polar molecule fluorophore interaction. However, the exciplex band was not resolvable into two components of solvated and unsolvated species; nor was there any isoemissive point in the exciplex spectra as a result of addition of polar molecules. In any event, the use of system (I) may have introduced some unknown quantities in the interactions, because: there is evidence that it interacts in the ground state with the added polar molecules; also, in a hydrocarbon medium, it shows a two-component emission - a monomer and an exciplex band, both of which are quenched by the added polar molecules.

The foregoing studies by Chandross and Thomas, and Beddard et al represent, to our knowledge, the only published work on the subject of "stoichiometric" complex formation between an exciplex and a polar molecule. Though their suggestion for a 1:1 interaction has not been clearly demonstrated experimentally, their results seem to have provided a strong basis for more investigation of the

subject. Besides, in their studies, little or no attempt was made to correlate the observed specific interaction with other properties of the polar molecule other than its bulk dielectric constant. For example, its donicity, which is a measure of the nucleophilic properties of the polar species, is expected to play a major role in solvating the positive end of the exciplex. Donicity is defined as the negative ΔH -value in kcal·mol⁻¹ for the 1:1 adduct formation between the reference acid $SbCl_5$ and the donor in the quasiinert solvent 1,2-dichloroethane.¹¹⁵ It has been shown that the dissociation constants of some ionic compounds in polar solvents of similar dielectric constants are dependent on the donor number (DN) of the polar solvent. For example, 116 the dissociation constants of quinuclidinium chloride (QHCl) are much lower in acetonitrile ($\varepsilon = 37.5$, DN = 14.1) and nitromethane ($\varepsilon = 36.67$, DN = 2.7) than in N,N-Dimethylacetamide, DMA ($\varepsilon = 37.78$, DN = 27.8) and N,N-Dimethylformamide, DMF (ε = 37, DN = 26.6) even though these solvents have similar dielectric constants. On the other hand, QHCl is equally strongly dissociated in DMF or DMA as in propanediol-1,2-carbonate, PDC (ε = 65, DN = 15.1) even though the latter solvent has a much higher dielectric constant and dipole moment. It is true that the dissociation constant of QHCl will also depend on the electrophilic property of the polar solvent; however, the observation that the dissociation constant of QHCl in acetonitrile
is considerably lower than in DMF (the former being a stronger electrophile, but a much weaker donor) appears to indicate that the influence of the nucleophilic effect is dominating.

However, the dissociative tendency of QHCl was found also to depend on the dielectric constant. It exhibits a higher dissociation constant in PDC than in acetonitrile although both solvents have essentially the same nucleophilic and electrophilic properties. This was ascribed to the higher Born solvation energy contribution in PDC which has a considerably higher dielectric constant.

In the case of an exciplex in a low dielectric medium, to which is added small amounts of a dipolar species, 'local' dielectric effect may contribute to the red-shift in exciplex emission band. This is because in solutions of polar substances in non-polar solvents, the attractive forces existing between dipoles are known to lead to the formation of aggregates of polar molecules.^{117,118} Such aggregates, if formed around the exciplex may create "local" dielectric effects.

Thus, in this chapter we will study the interaction of the intramolecular exciplex of 2,6-Bis(N dimethyl, methylamino)naphthalene, IV, with a number of polar species in order to examine the involvement of specific interaction and/or "local" dielectric effect in red-shifts generally observed in exciplex emission maximum as polarity of the medium is increased. An attempt will be made to

correlate exciplex <u>spectral shifts</u> with the <u>denicity</u> of the polar species in order to distinguish effects due to <u>specific interaction and polarity parameters</u>: The solventinduced fluorescent nature of the exciplex of IV, may be useful in making the above distinctions. Also, the closeness between the ground state and excited state geometries of IV may help to simplify the interaction of the exciplex with the polar molecules

Exciplex Fluorescence Spectra of 2,6-Bis(N-dimethyl, methylamino)naphthalene, IV, In Presence of Small Amounts of Polar Molecule

Small amounts of polar species were added successively to a dilute solution (1 x 10^{-4} M/L) of IV in ether; the room temperature absorption and emission spectra were obtained after each addition. The following polar species were used: ethyl alcohol, methyl alcohol, dioxane, methylcyanide (MeCN), N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSC) and hexamethylphosphoramide (HMPA).

The addition of any of the polar molecules caused no detectable change in the absorption spectra of IV in ether as solvent.

However, with the exception of dioxane, the addition of small amounts of ethyl alcohol, methyl alcohol, MeCN, DMF, DMSO and HMPA, caused significant red-shifts in the exciplex emission maximum in IV. This is illustrated in Figure 7.1 for the case of DMSO. The isoemissive point, observed in all cases, does not seem real since it shifts to longer wavelength with increase in concentration of the polar molecule.

No change in exciplex band shape is observed; instead there is a more or less symmetrical broadening of the peak.

Also, exciplex fluorescence quantum yield (0.011) stays constant on addition of small amounts of polar molecules, for example ~ 0.05 M (DMSO), ~ 0.24 M (DMF) and ~ 0.10 M (MeCN); then it decreases only slightly at higher concentrations.

The extent of the red-shift of exciplex emission band is dependent on the nature of the polar molecule. We will compare the interactions, involving only nonprotic polar species, in order to eliminate effects due to hydrogen bonding. Thus a comparison of exciplex emission spectra (Figure 7.2) obtained by adding the same amount (0.05 M) of polar species, shows a red shift which increases in the order: HMPA > DMSO > DMF > MeCN. However, as the concentration of the added polar molecule increases, the amount of red-shift caused by DMSO becomes slightly larger than that caused by HMPA (Figure 7.3). It may be noted that acetonitrile causes no shift in exciplex band for concentrations less than ~ 0.02 M. The effect of dioxane is very slight - causing a red shift of ~ 3.6 nm at a concentration of 0.4 M.



Figure 7.1. Fluorescence spectra of IV in ether, in the presence of varying amounts of DMSO (moles/ litre): --0.02 (a), 0.11 (b), 0.31 (c); --0.02 (a), 0.16 (b), 0.56 (c); ---0.04(a), 0.21 (b), 0.72 (c); ---0.07 (a), 0.26 (b), 0.94 (c); ... 0.09 (a), 0.31 (b), 1.18 (c). λ_{ex} 290 nm.







A plot of exciplex spectral shift as a function of donor number of the polar molecule is given in Figure 7.4. At relatively low concentrations of added polar molecule $(\tilde{>}0.05 \text{ M})$, the red shift in exciplex emission maximum appears linearly dependent on the donor number; thus the extent of shift increases in the order HMPA > DMSO > DMF > MeCN. However, at relatively higher concentrations (for example 0.29 M), some deviation to the above linearity occurs for polar molecules that differ widely in dielectric constant; hence the observed red shift by DMSO becomes greater than that of HMPA.

A plot of exciplex spectral shift as a function of bulk dielectric constant is shown in Figure 7.5. The bulk dielectric constant, ε , of the medium (mixture of the solvent and added polar molecule) is estimated from the expression:¹¹³

$$\varepsilon = V_{\dagger}\varepsilon_{\dagger} \tag{7.1}$$

where V_1 is the volume fraction of solvent (ether) or the polar molecule, and ε_1 is the dielectric constant of the pure solvent or pure polar molecule. Figure 7.5 shows that at a given bulk dielectric constant, the magnitude of the red-shift increases in the order HMPA > DMSO \approx DMF > MeCN. It is to be noted also that at bulk dielectric constant of 4.40 for the mixture ($\varepsilon = 4.335$ for pure solvent) HMPA causes a finite red shift of ~ 2.4 nm, while DMSO, DMF and



Exciplex spectral shift as a function of donor numbers. Concentration of polar molecule (moles/litre): (\bigcirc) 0.05, (\triangle) 0.29. Figure 7.4.





MeCN cause no detectable shift. Above $\varepsilon = 4.40$, all but MeCN bring about spectral shift, the latter showing detectable red shift from $\varepsilon \sim 4.5$.

Onset and Growth of Fluorescence of Intramolecular Exciplex of IV

We saw in Chapter 6 that compound IV gives intramolecular exciplex fluorescence in moderate to highly polar solvents, such as diethylether, methylene chloride, ethyl alcohol and acetonitrile; while in hydrocarbon solvents only monomer emission is observed, though with substantial quenching. However, compound IV does give an intense intramolecular exciplex fluorescence in dioxane ($\varepsilon = 2.209$). Thus, the non-observance of exciplex fluorescence in hydrocarbon solvents, such as methylcyclohexane ($\varepsilon = 2.02$) seems not to be dependent on solvent polarity parameters alone. Since compound IV acquires a dipolar character in the excited state due to charge transfer (CT) interaction, it could therefore interact in a specific manner with surrounding polar solvent molecules. Such an interaction may be revealed by studying the emission spectra of a hydrocarbon solution of IV in the presence of small amounts of a polar molecule.

The above experiment was carried out, using methylcyclohexane as the solvent, and N,N-Dimethylformamide (DMF), methyl cyanide (MeCN) and Dimethylsulfoxide (DMSO) as the polar molecules. Addition of small amounts of DMF and MeCN led to the appearance and growth of intramolecular exciplex fluorescence in IV, and quenching of monomer fluorescence. The polar-molecule-induced exciplex emission undergoes a red shift as concentration of polar molecule is increased. The case of DMF is shown in Figure 7.6. Addition of one drop (~ 0.08 M) of DMSO to a dilute solution of IV in methyclohexane gave a two component emission band, consisting of a monomer and an exciplex emission band, and similar to that obtained with one drop of DMF (0.07 M) (Figure 7.6). However, additional drops of DMSO remained immiscible with methylcyclohexane; so that the I_E/I_M ratio remained constant at a value of ~ 0.86 .

A plot of the ratio of exciplex and monomer fluorescence intensities, I_E/I_M against concentration of polar molecule is shown in Figure 7.7 for MeCN and DMF. At any given concentration, a greater I_E/I_M ratio is obtained for DMF than for MeCN.

Also, a plot of I_E/I_M ratio against bulk dielectric constant, ε (estimated from Equation 7.1) is shown in Figure 7.8. For $\varepsilon < 2.525$, DMF shows higher I_E/I_M ratios than MeCN; this trend is reversed for $\varepsilon > 2.525$. Also, while MeCN gives zero I_E/I_M ratio at $\varepsilon \sim 2.035$, DMF gives a finite I_E/I_M ratio of 0.16 at $\varepsilon = 2.0$, which is slightly below the bulk dielectric constant of the methylcyclohexane ($\varepsilon = 2.02$).











Ratio of intensities of monomer and exciplex fluorescence as a function of bulk dielectric constant (\bigcirc) DMF, (*) MeCN. Figure 7.8.

Discussion

The observed red-shifts in exciplex emission maximum on addition of small amounts of MeCN, DMF, DMSO and HMPA may be explained by considering the contributions of the following molecular properties:

bulk dielectric constant;

donicity; and

"local" dielectric constant.

According to the usual solvation theory, 54,119,120 the red shift in the exciplex emission band with increasing solvent polarity is considered to arise from solvation of the highly polar exciplex by a bulk dielectric continuum. This solvation theory neglects specific interaction between the exciplex and the surrounding polar molecules. Thus, the exciplex fluorescence energy is treated as a direct function of polarity parameters. On this premise, one would expect that, by adding equal amounts of the polar molecules: MeCN (ε = 37.5), DMF (ε = 37.0), DMSO $(\varepsilon = 46.68)$ and HMPA $(\varepsilon = 30.0)$, the extent of red-shift will be: DMSO >> MeCN \approx DMF > HMPA. However the observed order: HMPA ≈ DMSO > DMF >> MeCN contradicts the above order expected on the basis of bulk dielectric effect. Furthermore, if exciplex energy in solution is purely dependent on bulk dielectric constant of the medium, then its energy will be the same in different media of the same

bulk dielectric constant. However, our results (Figure 7.5) indicate that addition of different amounts of the above polar molecules to give the same bulk dielectric constant, leads to different amounts of red-shifts in the exciplex emission maximum. Again the observed order: HMPA > DMSO \approx DMF > MeCN does not reflect any polarity effect. In fact the least polar HMPA is seen to produce the highest spectral shift under both conditions of the same bulk dielectric constant and the same amount of added polar molecule. For DMF and MeCN which have similar bulk dielectric constant, the former causes relatively higher red shifts.

The observed red shifts in exciplex emission maximum appear rationalizable on the basis of the donor number (DN) of the polar molecule: HMPA (DN = 38.8), DMSO (DN = 29.8), DMF (DN = 26.6) and MeCN (DN = 14.1). Thus, at low concentrations of added polar molecule (<0.05 M) the observed order of red shift is HMPA > DMSO > DMF >> MeCN (Figures 7.3 and 7.4). At relatively high concentrations (>0.05 M) of polar molecules of similar dielectric constants, the observed red shift is still largely dependent on donicity, hence the order: HMPA > DMF > MeCN. Under the condition of the same bulk dielectric constant of the medium, the observed order of red shift: HMPA > DMSO \approx DMF > MeCN, again lends support to the influence of donicity. The equality of the red-shifts by DMSO and DMF can be understood from the similarity of their donor

numbers.

Also the higher values of $I_{\rm E}/I_{\rm M}$ ratio obtained with DMF compared to those of MeCN, seem indicative of the effect of donicity. On the basis of bulk dielectric effect, both polar molecules are expected to have similar intensity ratios. From the plot of $I_{\rm E}/I_{\rm M}$ ratio against bulk dielectric constant (Figure 7.8) DMF has a finite $I_{\rm E}/I_{\rm M}$ ratio at a bulk dielectric constant that is slightly less than that of the pure hydrocarbon solvent, in which exciplex fluorescence is not observed. One implication of this is that the non-occurrence of intramolecular exciplex fluorescence of IV in hydrocarbon solvents is probably not due to their low dielectric constant alone, but also may result from their non-nucleophilic character. This seems to be true, because compound IV exhibits intense intramolecular exciplex fluorescence in dioxane which is essentially nonpolar ($\varepsilon = 2.209$), but has a moderate nucleophilic character (DN = 14.8).

The overall implication of the foregoing correlation of the red shift in exciplex emission maximum with the donicity of the polar molecule is that the electrostatic interaction between an exciplex and a polar molecule could be specific in nature, and may lead to a 1:1 or 1:n complex formation. Obviously, the positive charge on the exciplex which is localized on the nitrogen, is susceptible to solvation by nucleophilic polar molecules. The

continuous decrease in exciplex energy with increase in concentration of the polar molecule appears to favor a loose multi-component complex, involving one exciplex moiety (or an excited state molecule of IV) and many polar molecules. This seems to be the case since there is no real isoemissive point, and no detectable change in exciplex band shape.

In spite of the overwhelming evidence in favor of the specificity of the interaction of an exciplex with a polar molecule, particularly at low concentrations of the latter, dielectric effects seem to be evident at concentrations above ~ 0.05 M (Figure 7.3). Thus the red shift caused by DMSO is relatively higher than that of HMPA in the above region of concentration. Also, dielectric effect seems to account for the deviation observed at relatively high concentration (0.29 M) in the plot of exciplex spectral shift as a function of donor number (Figure 7.4). Furthermore the fact that small amounts of methylcyanide (DN = 14.1) do bring about red shifts in exciplex emission maximum in ether (DN = 19.2) as solvent, appears to show that dielectric effects do not seem altogether negligible, even at the so called low concentrations of the polar molecule. If the red shift occurs only by specific interaction which in turn appears dependent on the donicity of the polar molecule, then a 'levelling effect' would have been observed in the case of MeCN.

It is possible for the added polar molecules to form aggregates in the comparatively non-polar solvent.^{111,112} Such aggregates can be formed around the exciplex because of its highly dipolar character. As the concentration of the polar molecule increases, the surface area of aggregation increases, and this may lead to a "local" dielectric effect on the central dipole (exciplex). The 'local' dielectric effect will gradually lead to a bulk dielectric effect at very high concentrations of polar molecule. This seems to explain the continuous lowering of exciplex energy (with increase in concentration of polar molecule) to a final value that will be observed in the particular pure polar medium.

We may compare an exciplex with its surrounding polar molecules in a non-polar medium with a hydrocarbon monomer trapped inside a micelle of emulsifier molecules in an aqueous (polar) medium. The surface area of this micelle is known to increase with increase in concentration of the emulsifier, and this leads to increased solubilization of the non-polar solute (monomer) in water. In the same manner increased stabilization of the polar solute (exciplex) in a non-polar medium will be expected with increase in surface area of aggregates of polar molecules, which may be considered 'emulsifier' agents. This will correspond to a loose l:n complex between the exciplex and the added polar molecules.

In conclusion, it appears that the red shift in exciplex emission maximum observed in polar media occurs by a <u>combination of specific interaction</u> and <u>orientation</u> <u>polarization interaction</u> (dielectric effect). The contribution of the former will probably depend on the nucleophilic properties (dcnicity) of the solvent, and will be effective at short range, preceeding the dielectric effect. Also the observed red shift in exciplex emission maximum in the presence of small amounts of a polar molecule in a non-polar medium appears explicable on the basis of both specific interaction and "local" dielectric effect. The latter is believed to result from aggregation of polar molecules in a non-polar medium.

CHAPTER 8

EXPERIMENTAL

I. Synthesis

General Procedure

All melting points were determined with a Thomas Hoover melting point apparatus in open capillaries.

A Varian T-60 spectrometer was used to record nmr spectra, which were recorded as δ values in ppm downfield from an internal standard of tetramethylsilane.

Mass spectra were obtained by Mr. Mark M. Weidner on a Hitachi Perkin Elmer RMU-6 mass spectrometer.

Microanalyses were performed by Span Microanalytical Laboratory, Eagle Harbor, Michigan.

Viscosity measurements were performed using a Cannon (75, A32) viscometer.

2,6-Bis(bromomethyl)naphthalene (3)



Following Golden's procedure,⁵⁸ a mixture of 120 g (0.77 moles) of 2,6-dimethylnaphthalene and 0.70 g of benzoyl peroxide in 1.4 liters of benzene (dried over CaH) was refluxed and mechanically stirred in a 2 litre round bottom flask. Then a mixture of 300 g (1.7 moles) of Nbromosuccinimide (NBS) and 3.5 g of benzoyl peroxide was added in four equal portions, over a period of 55 minutes. Refluxing was continued for another one hour.

The hot solution was filtered. The benzene filterate, on standing, gave a solid, product-1, which was treated with 0.25 M sodium hydroxide to destroy any succinimide. Product 1, on recrystallization with a 1:3 mixture of chloroform and tetrahydrofuran, gave 35.86 g of colorless rodlike crystals. mp 182-185° (lit.^{59,121} 182-184°).

The residue from the filtered hot reaction mixture weighed 226.07 g (expected yield of succinimide was 152.3 g). This residue was then digested with two 750 ml portions of benzene to yield product 2; recrystallization with CHCl₃/THF mixture gave colorless rod-like crystals which weighed 39.89 g. mp 182-185°. Final weight of succinimide was 141.45 g.

Over-all yield of product was 75.59 g (31.4%).

2,6-Bis(methylamino)naphthalene,(6)

6

6.0 g (0.02 moles) of 2,6-bis(bromomethyl)naphthalene was put in a l-litre round bottom flask equipped with a cold finger; 300 ml of ethyl alcohol (absolute) was added, and the mixture stirred with a magnetic stirrer. To this mixture was added 76 ml (\sim 3.13 moles) of ammonia dissolved in 100 ml of ethyl alcohol (absolute). The reaction flask with its contents was then heated to a temperature of 30° and the reaction mixture refluxed by means of the cold finger maintained with a dry ice/isopropanol mixture. The inhomogeneous reaction mixture turned milky after 15 minutes; heating was stopped after 25 minutes to minimize the escape of NH₃ gas from the system. The reaction was then left to run at room temperature for 21 hours.

The reaction mixture remained milky. Filteration yielded a pale white solid (0.321 g) and a clear filtrate. The filtrate was left to stir for 24 hours in an open beaker to expel excess NH_3 gas; a white residue (the hydrobromide salt of the amine) was obtained (4.85 g).

The above residue was converted to the free amine by treating its solution in 0.1 NHCl solution with 1 N NaOH;

the resulting solid amine was recrystallized with a 1:3 mixture of methylene chloride and cyclohexane to give a white fluffy powder (2.04 g, 57.4%), mp 125-130°. nmr (CDCl₃/TMS) δ 7.27-7.72 (s,aromatic), δ 3.95 (Ar·CH₂), δ 1.58 (-NH₂) mass spectrum (70 eV): base peak at M/e 186 (parent), M/e 185 (P-1, 90%, M/e 170 (P-NH₂, 63%), M/e 156 (P-CH₂NH₂, 51%).

2,6-Bis(N-methyl,methylamino)naphthalene, (8)



10 g (0.032 moles) of 2,6-bis(bromomethyl)naphthalene was put in a 2-litre round bottom flask, equipped with a cold finger. 460 ml (~10.37 moles) of methylamine dissolved in 400 ml of absolute ethyl alcohol, was added into the flask, and the mixture refluxed by heating to a temperature of 45°, and cooling with a dry ice/isopropanol mixture in the cold finger. Stirring was done by means of a magnetic stirrer.

A clear solution resulted after about 30 minutes; refluxing was continued for two hours. On evaporation of ethanol and excess methylamine, a white needle-like crystalline solid was recovered. This was dissolved in 0.5 N HCl solution, and treated with 1 N NaOH in a selective two-stage precipitation process that yielded the product (secondary amine) as the final precipitatewhite silvery flakes. The product was then recovered by suction filtration, and vacuum dried at 42°C to constant weight (5.905 g, 86%). mp 52-60°. nmr (CDCl₃/TMS) $\delta7.22-7.72$ (aromatic), $\delta3.8$ (Ar·CH₂-), $\delta2.43$ (NCH₃), $\delta1.4$ (NH).

Anal. Calcd. for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47. Found: C, 77.85; H, 8.02. mass spectrum (70 eV): base peak at M/e 42 ($\dot{C}H_2$ -N=CH₂), M/e 214 (parent, 64%), M/e 184 (P- $\dot{N}HCH_3$, 37%), M/e 154 (P-2 $\dot{N}HCH_3$, 33%) M/e 44 ($\dot{C}H_2NHCH_3$, 82%).

2,6-Bis(N-dimethyl, methylamino)naphthalene, (10)



5 g (0.016 moles) of 2,6-bis(bromomethyl)naphthalene was put in a 1-litre round bottom flask equipped with a cold finger. 100 g (2.218 moles) of anhydrous dimethylamine was added into the flask. The mixture was heated to 45° and refluxed for two hours.

The clear reaction mixture was transferred to an open vessel, and stirred at room temperature to evaporate excess dimethylamine. A white finely crystalline solid was obtained (the hydrobromide salt of the tertiary amine). This was dissolved in 0.05 N HCl, and on treatment with 1 N NaOH solution some slight precipitation occurred (this was filtered off); further addition of NaOH, gave heavy white flakes (product). The solid free amine was recovered by suction filtration, washed with de-ionized water and dried in a vacuum oven at 40° to constant weight (3.29 g, 85.3%). mp 100-103°. nmr (CDCl₃/TMS) δ 7.23-7.72 (aromatic), δ 3.5 (Ar·<u>CH</u>₂-), δ 2.25 (-N(CH₃)₂). Anal. Cald. for C₁₆H₂₂N₂: C, 79.29; H, 9.15. Found: C, 79.26; H, 9.13. mass spectrum (70 eV): base peak at M/e 58 ($\dot{CH}_2N(CH_3)_2$), M/e 242 (parent, 41%), M/e 198 (P- $\dot{N}(CH_3)_2$, 50%), M/e 154 (P- $2\dot{N}(CH_3)_2$)

2,6-Bis(N-methyl, N-acetyl, methylamino)naphthalene, (1)



In a 250 ml 3-necked round bottom flask was placed 0.734 g (0.0094 moles) of acetyl chloride dissolved in 85 ml of chloroform. 1 g (0.0047 moles) of 2,6-bis(N-methyl, methylamino)naphthalene was dissolved in 60 ml of chloroform and added dropwise to the acetylchloride solution from

a separatory funnel, with stirring. There was some milky precipitation (probably hydrochloric acid salt of the amineexcess of which was used as acid acceptor). Stirring was continued at room temperature for 20 minutes; the milky reaction mixture was then suction filtered. The filtrate was washed with two 20 ml portions of 0.5 N HCl solution (to remove any unreacted amine), and then with two 20 ml portions of water. After drying with anhydrous sodium carbonate, the filtrate was evaporated to dryness to give a solid residue. Recrystallization with a mixture of ether and chloroform gave colorless plate-like crystals (0.343 g, 49.3%) mp 202-204°: nmr (CDCl₃/TMS) 67.22-7.75 (aromatic); $\delta4.60$ and 4.67 (Ar·<u>CH</u>₂-), $\delta2.90$ and 2.95 (NCH₃); $\delta2.17$ (-CCH₃). Anal. Calcd. for C₁₈H₂₂N₂O₂: C, 72.45; H, 7.43. Found: C, 72.06; H, 7.22 mass spectrum (70 eV): base peak at 225 (P-HNCOCH₃); M/e 298 (parent, 18%), M/e 255 (P-ĊOCH₃, 48%), M/e 226 (P-NCOCH₃, 51%). СН₃

Poly(2,6-dimethylenenaphthalene, N,N'-dimethyl succinimide), P2-14



An aqueous solution of the diamine-2,6-bis(N-methyl, methylamino)naphthalene (8) was prepared as follows: 3 g (0.014 moles) of (8) was dissolved in 80 ml of 0.5 N hydrochloric acid solution, and then neutralized with 1 N sodium hydroxide solution. The resulting diamine aqueous solution was diluted to 410 ml with distilled water and then transferred to the reaction vessel (a 1-litre 3-necked round bottom flask equipped with a mechanical stirrer, and a 250 ml separatory funnel). 2.25 g (0.056 moles) of sodium hydroxide was dissolved in 50 ml of distilled water and put in the separatory funnel. 4.35 g (0.028 moles) of succinyl chloride was dissolved in 250 ml of chloroform in a beaker, and then quickly added to the stirred diamine solution in the reaction vessel. The separatory funnel was simultaneously opened to let in sodium hydroxide solution (acid acceptor).

The reaction mixture turned milky instantaneously; stirring (controlled with a Variac set at 90V) was continued for fifteen minutes. The reaction mixture was then transferred to a 500 ml separatory funnel, to separate the aqueous layer (clear) from the chloroform layer (slightly colored brown).

Recovery and purification of the polymer was effected as follows: the chloroform layer (containing the polymer) was reduced to about 50 ml of volume, and the polymer precipitated by addition of methyl alcohol (a non-solvent)

with stirring. Product (recovered by suction filtration) was slightly colored brown; it was then re-dissolved in a small amount of chloroform, and the precipitation with methyl alcohol was repeated two more times; a white powdery product was obtained (1.836 g, 44%). mp 115-125°. nmr (CDCl₃/TMS) δ 7.27-7.73 (aromatic), δ 4.68 (Ar·<u>CH</u>₂-), δ 2.77 and 2.95 (>NCH₃), δ 1.83 (-CCH₂0). Anal. Calcd. for C₁₈H₂₀N₂O₂: C, 72.95; H, 6.80. Found: C, 70.42; H, 6.48.

Poly(2,6-dimethylenenaphthalene,N,N'-dimethyladipamide), P4-14



A 150 ml aqueous solution of 0.5 g (0.002 moles) of 2,6-bis(N-methyl, methylamino) naphthalene was made as in $P2-\frac{14}{2}$. 0.584 g (0.0032 moles) of adipyl chloride, dissolved in 100 ml of chloroform was then interfacially polymerized with the aqueous diamine solution in the presence of 0.265g (0.007 moles) of sodium hydroxide, as the acid acceptor. The reaction procedure, and the product recovery and purification were done as in $P2-\frac{14}{2}$. The pure product was a

white powder. (0.206 g, 27.0%) mp 193-195°. nmr (CDCl₃/TMS) δ 7.27-7.72 (aromatic), δ 4.65 (Ar \cdot <u>CH</u>₂-), δ 2.87 (>NCH₃), δ 2.38 (b,-CCH₂-), δ 1.78 (b,-C \cdot CH₂ $(<u>CH</u>₂)₂CH₂<math>\cdot$). Anal. Calcd. for C₂₀H₂₄N₂O₂: C, 74.04; H, 7.46. Found: C, 71.26; H, 7.37.

Poly(2,6-Dimethylenenaphthalene,N,N'-dimethylsuberamide), P6-14.



Using the experimental procedure of P2-14, 0.6 g (0.0028 moles) of 2,6-bis(N-methyl, methylamino)naphthalene, g(in 90 ml of distilled water) was interfacially polymerized with 0.652 g (0.003 moles) of suberoyl chloride (in 60 ml of chloroform) in the presence of 0.247 g (0.0062 moles) of sodium hydroxide (acid acceptor).

Repeated attempts to precipitate the polymer from its chloroform solution with methanol, failed. Use of hydrocarbon non-solvents led to a rubbery material - slightly colored brown; this was treated with methyl alcohol to disperse the bulky material into fine particles; on filtering and drying a slightly off white powder was obtained (0.02578 g, 2.6%) mp 115-126° nmr (CDCl₃/ TMS) δ 7.30-7.70 (aromatic), δ 4.63 (Ar·<u>CH₂</u>-) δ 2.87 (=NCH₃)

$$\delta 2.33 (b_{-CCH_{2}-}), \delta 1.47 \text{ and } 1.67 (b_{-C} \cdot CH_{2} + CH_{2} + CH_{2} \cdot CH_{2}).$$

Poly(2,6-dimethylenenaphthalene,N,N'-dimethylsebacamide), P8-14



Using the experimental procedure of P2-14, 0.5 g (0.0023 moles) of 2,6-bis(N-methyl, methylamino)naphthalene (in 110 ml of distilled water) was interfacially polymerized with 1.12 g (0.0047 moles) of sebacoyl chloride (dissolved in 100 ml of carbon tetrachloride). 0.378 g (0.009 moles) of sodium hydroxide was used as acid acceptor.

A solid rubbery material (slightly brownish) was recovered from the reaction mixture. Purification was effected by twice dispersing into fine particles with methyl alcohol; after drying (in a vacuum oven) a creamy white powder was obtained (0.265 g, 30%), mp 123-125°. nmr (CDCl₃/TMS) δ 7.30-7.70 (aromatic), δ 4.64 (Ar·<u>CH</u>₂-), δ 2.9 (>NCH₃), δ 2.37 (b, -C·CH₂-), δ 1.33 and 1.70 (b,-C·CH₂(<u>CH</u>₂)₆CH₂·G-). Anal. Calcd. for C₂₄H₃₂N₂O₂: C, 75.75; H, 8.48. Found: C, 74.61; H, 8.30. Attempted Synthesis of Poly(2,6-dimethylenenaphthalene, N,N'-dimethyl Glutaramide), P3-14



Using the experimental procedure of P2-14, 1 g (0.00467

moles) of 2,6-bis(N-methyl, methylamino)naphthalene (in 160 ml of water) was interfacially polymerized with 0.878 g (0.00514 moles) of glutaryl chloride (dissolved in 80 ml of chloroform. 0.412 g (0.0109 moles) of sodium hydroxide was used as acid acceptor.

Attempts to recover the product by precipitation from chloroform using non-solvents (methanol and cyclohexane) failed. Evaporation of solvent gave a reddish brown rubbery product. No further attempt was made to purify the product; it was therefore not used in the photophysical studies.

II. Solvents for Luminescence Studies

Methylene chloride, chloroform, Methyl Alcohol, and 1-Butanol were spectroquality solvents by Mallinckrodt Chemical Works. <u>Acetonitrile, Cyclohexane, p-Dioxane, Methyl Sulfoxide and</u> <u>N,N-Dimethyl formamide</u> were spectroquality solvents from Matheson Coleman and Bell (MC/B).

Isopropanol was a "photrex" reagent by J. B. Baker Chemical Company.

Hexamethylphosphoramide was purchased from Aldrich Chemical Company, Inc., and was used without further purification.

<u>Diethyl ether (Ether)</u>. This was dried over lithium aluminum hydride (LiAlH), and distilled (when needed) through a l meter vacuum jacket column.

<u>Ethanol</u>. 200 proof ethanol was distilled through a 1 meter vacuum jacket column, at a slow rate (about 5 drops per minute). Portions of about 50 ml were collected, and the absorption spectrum taken in a 10 cm cell to check for benzene. Distillation was continued till the characteristic benzene UV absorption was no longer apparent. Ethanol was then distilled and used as needed.

<u>3-Methylpentane (3MP)</u>. A modified version of the purification method of Potts¹²² was used. 3-methylpentane (Phillips Pure Grade) was shaken for 30 minutes with a 50:50 mixture of concentrated sulfuric acid and concentrated nitric acid. It was then shaken 3 times for 30 minutes each with concentrated sulfuric acid. This was then treated with sodium carbonate solution until the CO₂ production ceased. The 3MP was then washed several times with water until the water remained clear compared to the yellow color of the first wash. The 3MP was stored over sodium ribbon in a flask over night. It was refluxed through a vacuum jacketed 1 meter column and distilled for use as needed.

III. Spectral Measurements

<u>Absorption Spectra</u>. Cary 15 and Cary 17 were used to obtain absorption spectra.

<u>Emission Spectra</u>. Aminco-keirs and Aminco-Bowman spectrophosphorimeters were used to obtain fluorescence spectra. Also, the phosphorescence spectra were obtained with the above instruments equipped with a rotating can phosphoroscope.

Fluorescence Quantum Yields

Fluorescence quantum yields were determined by comparison with two standards of known quantum yields:

i) Quinine sulfate (l x 10^{-4} M/L in 0.1 NH₂SO₄. This was used to determine the relative quantum yields

of intramolecular <u>exciplex fluorescence of 2,6-bis(N-</u> <u>dimethyl, methylamino)naphthalene, IV, in organic solvents</u> <u>of different polarities</u> (Table 6.2). A quantum yield of 0.55 was assumed for Quinine sulfate.¹²³

ii) 2,6-Dimethylnaphthalene (1 x 10⁻⁴ M/L in the same solvent as the unknown). This compound was used to determine the relative quantum yields of <u>monomer fluorescence</u> <u>of 2,6-bis(methylamino)naphthalenes, II-IV</u> in 3-methyl pentane (Table 6.1); and <u>monomer and excimer fluorescence</u> <u>of the polyamides (P-2, P-4, P-6 and P-8) and model compound</u> in a 1:3 mixture of chloroform and ethanol (Table 4.1). A quantum yield of 0.3 was assumed for 2,6-dimethylnaphthalene.¹²⁴

This comparative method for quantum yield determination is based on Beer's law. For two optically dilute solutions, with fluorescence intensities F_1 and F_2 (measured under identical conditions) the following ratio holds:¹²³

$$\frac{F_1}{F_2} = \frac{\Phi_1 \varepsilon_1 C_1 \ell}{\Phi_2 \varepsilon_2 C_2 \ell} = \left(\frac{\Phi_1}{\Phi_2}\right) \left(\frac{\text{Optical density of } 1}{\text{Optical density of } 2}\right)$$
$$= \frac{\text{Area } 1}{\text{Area } 2}$$
(8.1)

where Φ is quantum yield, ε is molar extinction coefficient, C is concentration in moles per litre, ℓ is optical path length of sample cell, l and 2 refer to the standard and the unknown compound respectively. All spectral measurements were performed with dilute solutions of the unknown $(1 \times 10^{-4} \text{ M/L})$ in matched 1 cm square cells. Solutions were excited at 290 nm, at room temperature, and the fluorescence was viewed at right angle. The spectrum of the unknown was first recorded; then the standard was quickly inserted and its spectrum taken. The area under the spectra of both the standard and the unknown were carefully cut out and weighed.

Uncorrected spectra were used because of the close overlap of the spectra of the standards with those of the respective unknowns. However, refractive index corrections were made in the relative quantum yields determined with quinine sulfate (as standard) because the unknowns were dissolved in different solvents. These corrections were effected with the following expression:¹²⁵

$$\Phi_3 = \Phi_2 \left(\frac{n_1}{n_2}\right)^2 \tag{8.2}$$

where $n_1 (1.3341)^{25^{\circ}}$ is the refractive index of 0.1 N H_2SO_4 and n_2 is the refractive index of the organic solvent. Φ_2 is the uncorrected quantum yield obtained from equation (8.1), and Φ_3 is the quantum yield corrected for effects due to refraction of light.
IV. Fluorescence Life Time Measurements

Fluorescence decay times were measured by means of a <u>Single Photon Time Correlation Spectrometer</u>. This instrument consists essentially of a nanosecond flash lamp, a special photomultiplier for detecting individual photons, a time-to-amplitude converter (TAC) for timing the fluorescence photons relative to the flash lamp, and a multichannel analyzer (MCA) for data storage. A block diagram of the instrument is shown in Figure 8.1.

The nanosecond lamp is a relaxation oscillator where the voltage across two electrodes is increasing through charging a capacitor till the breakdown voltage of the gas filling the lamp (D_2 was used) is reached whereupon the lamp discharges and the circle is repeated. The width at half maximum (whm) intensity of the lamp was ~ 2 ns. The lamp flash is detected with the IP28 phototube, and the resulting analog pulse, after discrimination against lowlevel noise (Ortec Model 436) is used to start the TAC.

Fluorescence photons are detected by a fast photomultiplier 56 DUVP (Time Resolution 800 picoseconds). This phototube can amplify a single photon into an electrical pulse of several volts. This pulse is used to stop the TAC.

The time resolution of the apparatus depends upon the uncertainty of timing the detection of single-photon pulses relative to the flash-lamp pulse. The principal time



Figure 8.1. Block diagram for time resolved spectrophotometer.

jitter arises from the fact that the amplitude of singlephoton pulses is not constant but covers a broad range in pulse heights. The jitter associated with timing by a single-level crossing was eliminated by using a "constant fraction timing" discriminator (Ortec Model 463).

The heart of the instrument is the TAC (Ortec Model 457). Its operation is illustrated in Figure 8.2. Each time the lamp flashes, a pulse is sent to the TAC and initiates its time sweep (start). If during the time sweep a stop pulse is received from the photomultiplier, a TAC output pulse is generated with amplitude proportional to the time $(t_{stop} - t_{start})$.

The TAC is calibrated with the Ortec 462 Time Calibrator. The time base is a precision 100-MHz crystal-controlled oscillator that is calibrated against WWV, the National Bureau of Standards frequency, and it is temperaturecompensated for accuracy within the normal operating range of 0 to 50°C.

The output of the TAC is fed to the MCA. The MCA (Nuclear Data Model 1100) takes this voltage V and converts it to an appropriate channel number C. The final result is a count stored in Channel number C which is a record of the time at which the photon was observed by the photomultiplier. The analyzer channels now represent increments in time, and the counts in each channel are proportional to the probability for fluorescence emission from the sample between t and t+ Δ t, where t is measured from an arbitrary but





fixed point. Since the TAC seeks one photon after it is started, then each pulse of the lamp can produce only one count. By collecting many of these single photon events we eventually build in the analyzer the decay curve of the emitting species.

The contents of the memory of MCA can be displayed on an oscilloscope or an XY plotter or can be fed to a teletype equipped with a tape punch. Through the use of an accoustic coupler, the teletype is connected with the CDC 6500 computer where the data are processed. The processed data are plotted through a digital plotter (HEWLETT-PACKARD 7200A).

The lamp pulsing rate and the photon counting rate are monitored through two digital counters (Monsanto Model 150A). Monitoring the photon counting rate is important since at too high a count rate there will exist a significant probability that two photons will be counted while the TAC is involved in a sweep. Typically the lamp repetition rate was 50 KHz and the count rate <100 counts/sec.

According to the Convolution theorem, 126 the instrument output I(t) (when a fluorescence decay curve is measured) is given by

$$I(t) = \int_{0}^{t} G(\lambda) F(t-\lambda) d\lambda \qquad (8.3)$$

F(t) is the time dependence of the lamp distorted by the detection system, and is determined experimentally with a

scatterer at the wavelength of the exciting light. G(t) is the time response of the fluorescence system when excited with the delta pulse of light. To obtain the desired function G(t), Equation (8.3) is solved by a process called deconvolution. The various deconvolution techniques have been reviewed by Ware.¹²⁷

However, if the fluorescence decay is a simple exponential and is long-lived (compared to the lamp decay) the decay data can be processed by KINFIT, using the expression:

$$COUNTS = U(1)^{*}exp(-U(2)^{*}XX(1)^{*}nsec/ch)$$
(8.4)

$$RESID = CALC - XX(2)$$
(8.5)

where U(2) is the rate constant for fluorescence decay; XX(1) is the number of channels since t=0; U(1) is the pre-exponential constant (initial count), nsec/ch is nanosecond per channel (0.388 nsec) and XX(2) is the experimental count.

The experimental counts are stored in 128 channels; since the lamp pulse is of short duration (with a pulse width of $\sqrt{2}$ nsec) photon counts from its decay are stored in the earlier channels ($\sqrt{30}$). For the KINFIT analysis, we used counts from channel 68, in order to eliminate the lamp contribution in the fluorescence decay curve. Good fits were obtained between the experimental and the calculated points. A typical fit is shown in Figure 8.3. The KINFIT program used in these analyses is given in Appendix 8.1.



Appendix 8.1

.... TIMUE 35 TURN INUE 3 NTINUE TYTEN Chillmys Chilfhanse-1) GO TO 20 FTURN Ghilfhanse FTURN GTURN ETURN ETURN ETURN ETURN ETURN ETURN ETURN ETURN 5 29 . 10 11 9 NTINUE CONTINUE 12

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