# PART I

# RADIATIONLESS TRANSITIONS IN ORGANIC SYSTEMS-- DETERMINATION OF INTERSYSTEM CROSSING YIELDS IN FLUID SOLUTION

# PART II

# INTRAMOLECULAR ELECTRONIC ENERGY TRANSFER BETWEEN NON-CONJUGATED CHROMOPHORES IN SOME MODEL COMPOUNDS

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Ad majorem Dei gloriam.

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# ABSTRACT

## PART I

The efficiency of reaching the lowest triplet state after excitation into low excited singlet levels was determined for benzene, naphthalene, and other polycyclic aromatic hydrocarbons as well as for a number of carbonyl compounds and amines in fluid solution at room temperature. The determinations were accomplished by a chemical method in which the compound in question is used as a photosensitizer for the cis-trans isomerization of suitable olefins. Conditions are such that olefin molecules quench all triplet sensitizer molecules; the olefins subsequently undergo geometric (cis ⇄ trans) isomerization. The details of the isomerization reaction are known and a simple determination of the quantum yield for the sensitized isomerization leads directly to the quantum yield of sensitizer triplets.

From the data, intersystem crossing rates are estimated, as well as efficiencies and rates of radiationless triplet-to-ground-state transitions. Some information concerning the mode and importance of radiationless first-excited-state-to-ground-state transitions is also included, as well as a discussion of the results in terms of present theoretical treatments of radiationless transitions.

## PART II

Intramolecular transfer of both singlet and triplet electronic excitation in the Leermakers' Compounds, 4-(1-naphthylmethyl)-benzophenone (LI), 1-(1-naphthyl)-2-(4-benzoylphenyl)ethane (LII), and 1-(1-naphthyl)-3-(4-benzoylphenyl)propane (LIII) occurs and has been studied in some detail. In addition to emission spectroscopy, chemical methods for detecting, characterizing, and counting molecules in triplet states were employed.

In all three compounds, totally efficient transfer of triplet excitation from the benzophenone groups to the naphthalene moieties occurs, and at nearly the same fast rate ($k > 10^{10}$ sec$^{-1}$).

Transfer of singlet excitation from the naphthalene moiety to the benzophenone group is about 90% efficient in LI, 75% efficient in LII, and 85% efficient in LIII. The rate of the singlet energy transfers ($k \sim 10^{7}$ - $10^{8}$ sec$^{-1}$) are much slower than the rate of the triplet excitation transfer. The fluorescent emissions from the Leermakers' Compounds exhibit a quite different spectrum than that from 1-methylnaphthalene, and significant bathochromic and hyperchromic effects are noted in the absorption spectra of the compounds. The nature of singlet excitation transfer in the Leermakers' Compounds is quite complex, and large stereochemical effects no doubt exist. A discussion of the results in terms of the several presently accepted mechanisms for electronic energy transfer is included.

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# PART I

# RADIATIONLESS TRANSITIONS IN ORGANIC SYSTEMS--DETERMINATION OF INTERSYSTEM CROSSING YIELDS IN FLUID SOLUTION

# INTRODUCTION

Information regarding radiationless transitions in electronically excited polyatomic molecules is important to many fields. Besides photochemistry, photobiology and molecular spectroscopy, old fields like analytical chemistry and newcomers like laser technology, radiation chemistry and radiation damage require this information. In an early (1936) theoretical paper concerning radiationless transitions, Teller (1) states this about their importance:

> The crossing of potential curves or surfaces is important if reaction mechanisms are discussed, particularly if activated states are involved. Thus in photochemistry both the chemical yield and the fluorescence will depend on the question whether the molecules can get from a higher potential surface to a lower one, transforming in this way electronic excitation energy into kinetic energy of atoms and finally into heat.

Recently two very different theoretical treatments of radiationless transitions have been published by Gouterman (2) and Robinson and Frosch (3).

Despite this long and widespread interest, almost no quantitative data concerning radiationless transitions exists in the literature. This is not surprising since, until recently, information about radiationless paths was inferred from measurements of the yields and lifetimes of the radiative processes. Unless the total luminescence yield is near unity, the interpretation of these data is ambiguous, and besides, experimental difficulties have prevented highly accurate measurements of luminescence yields.

A brief discussion of these indirect methods and their results, and of some ingenious new approaches follows. For purpose of discussion throughout this work, reference will be made to the Jablonski diagram shown in Figure I. This diagram represents a generalized molecule and nearly all the processes discussed can be schematically illustrated by its use.

## Internal Conversion

In molecular electronic spectroscopy "internal conversion" is defined as the rapid radiationless combination of electronic states of like multiplicity (4), path 2 in Figure I. In the gas phase, excitation of a molecule to high electronically excited states followed by internal conversion often leads to rupture of the molecule (5). In condensed phase, where vibrational relaxation is much faster ($10^{12}$ $sec^{-1}$), the molecule quickly proceeds to the lowest excited levels. Since many molecules fluoresce, path 4 in Figure I, at rates of $10^6$-$10^9$ $sec^{-1}$, radiationless transitions, path 3, between the lowest excited singlet level and the ground level must be slow compared to internal conversion between excited levels. These facts have been realized for a long time and are summarized in

Jablonski Diagram

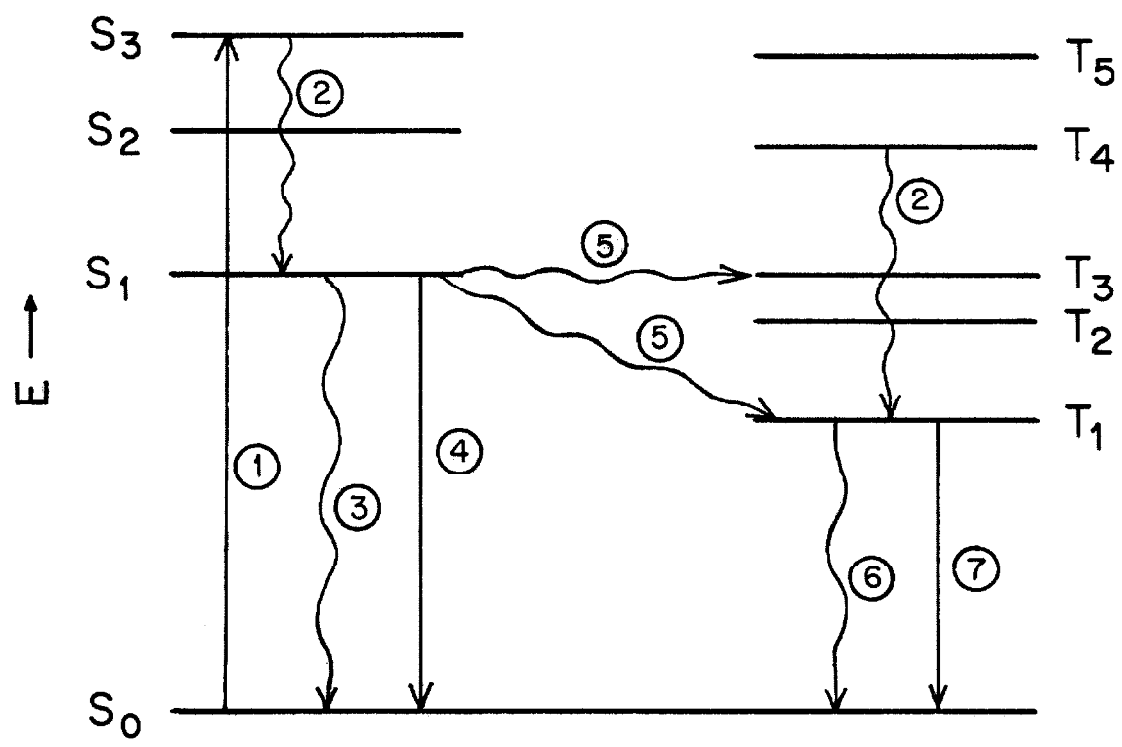

FIGURE I

$S_0$ is the ground (singlet) state

$S_1$, $S_2$, . . . , $S_n$ are excited singlet states

$T_0$, $T_1$, . . . , $T_n$ are excited triplet states

Straight arrows represent radiative transitions; wavy arrows represent radiationless transitions.

Kasha's rule (4): The emitting level of a given multiplicity is the lowest excited level of that multiplicity.* The rationale for this behavior is the relative spacings of the energy levels, the spacing between excited levels being almost always much smaller than that between the lowest excited levels and the ground state (4). A more accurate explanation (2, 3) will be discussed later. Whether, in condensed phase, excitation of a molecule to high electronically excited singlet states is followed by deactivation paths which do not lead through the first excited singlet states will be briefly discussed in other sections. Except where this question is specifically discussed, the highest lying state considered in this work will be the lowest excited singlet state ($S_1$).

## Intersystem Crossing

"Intersystem crossing" has been defined as the spin-orbital coupling dependent internal conversion in molecules (4). In this discussion intersystem crossing is, more clearly, a radiationless transition between two states, one of which is a singlet and the other a triplet.

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* In condensed phase azulene provides the only exception to this rule, since it fluoresces from its second excited singlet level and not from its first (6). This is no doubt due to its exceptional energy level spacings (3, 4). Naphthacene was believed to phosphoresce from its second triplet ($T_2$) state (7), but it was recently demonstrated (8) that the anomalous emission was phosphorescence from 5, 12-naphthacene quinone present as an impurity.

Many compounds phosphoresce, path 7 in Figure I, in viscous media especially at low temperature if they are excited to their lowest excited singlet states. Thus, intersystem crossing from $S_1$ to a triplet level leading, after internal conversion, to production of the lowest triplet state, competes with other deactivation paths leading from $S_1$ ($10^6$-$10^9$ $sec^{-1}$). In Figure I, paths 5 show intersystem crossings from $S_1$ to a triplet level closer to it, and directly to $T_1$. A discussion of the relative efficiencies of production of $T_1$ in these two ways will be found in a later section.

Phosphorescent lifetimes vary from $10^{-4}$ to 10 sec, so that intersystem crossing from the lowest triplet to the ground state (path 6 in Figure I) must be much slower than intersystem crossing from $S_1$ to the triplet manifold. The rationale here is the same as that given for multiplicity allowed radiationless transitions, namely that the energy gap between the vibrationless levels is much larger for the $T_1 \rightarrow S_0$ transition than for $S_1 \rightarrow T_2$, etc. transitions.

At this point, for purposes of later discussion, a terminology will be established for the radiationless deactivation paths. Starting with a molecule in the $S_1$ state, radiationless deactivation to the ground state will be called the radiationless $S_1 \rightarrow S_0$ transition to differentiate from the faster $S_{1+n} \rightarrow S_1$ internal conversions. Radiationless population of $T_0$ from $S_1$ will be called intersystem crossing without regard to the detailed path. The radiationless deactivation of the lowest triplet state to the ground state will be called the radiationless $T_1 \rightarrow S_0$ transition. Finally, the quantum yield of triplets, $\varphi_{ic}$, or the intersystem crossing yield, is the number of triplets $(T_0)$ produced per number of quanta absorbed producing $S_1$.

## The "Intersystem Crossing Ratio"

The first attempt to estimate intersystem crossing yields for organic systems from emission studies was made by Kasha (4, 9). He assumed that the radiationless $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transitions were unimportant in most cases, especially at low temperatures in highly viscous media. That is, an excited molecule will either fluoresce or phosphoresce under these conditions, $\varphi_p + \varphi_f \approx 1$. Thus, the rates of phosphorescence to fluorescence defined as the "intersystem crossing ratio," X, and easily determined from the total emission spectrum of the compound under steady excitation could be equated to the ratio of the rates of intersystem crossing and fluorescence, equations 1 and 2. Since the

$$X = \varphi_p / \varphi_f = \frac{k_{ic}}{k_f} \tag{1}$$

$$\frac{1}{X} + 1 = \frac{k_f + k_{ic}}{k_{ic}} = \frac{1}{\varphi_{ic}} \tag{2}$$

absolute rate of fluorescence could be estimated from the absorption spectrum, the absolute rate for intersystem crossing could also be estimated.

It was not long before measurements of the yields of total emission, fluorescence and phosphorescence were undertaken, and it became evident that for most organic molecules the total emission yield, even at very low temperatures, is significantly less than unity. Therefore, Kasha's intersystem crossing ratios are ambiguous in these cases.

## Emission Yields

The measurement of emission yields is both difficult and tedious and, in general, the results have not been very accurate. The earliest extended study of emission yields was that of Bowen and Williams (10). They studied fluorescence yields in hexane at room temperature. Some of these pioneering data, most of which are unreliable, are shown in Table I. With the development of low temperature techniques, sensitive and reliable photoelectric devices, and recording electronics, measurements of relative emission yields became much easier and more accurate, but absolute determinations still remain questionable. The most often quoted values for samples in EPA (ether:isopentane:alcohol 5:5:2) at 77°K are those of Gilmore, Gibson, and McClure (11). Their

### TABLE I. Emission Quantum Yields

| Investigator:[a, d] | A[b] |  | B[b] |  | C[c] |  |
|---|---|---|---|---|---|---|
|  | $\varphi_p$ | $\varphi_f$ | $\varphi_p$ | $\varphi_f$ | $\varphi_p$ | $\varphi_f$ |
| Compound: |  |  |  |  |  |  |
| Naphthalene | .10(.08) | .55(.44) | .05(.04) | [.55](.44) | .03(.04) | .29(.38) |
| Benzene | .25(.20) | .25(.20) |  |  |  |  |
| Triphenylene | .53(.43) | .04(.03) |  |  |  |  |
| Phenanthrene |  |  |  |  | .14(.18) | .12(.16) |
| Anthracene |  |  |  |  |  |  |
| Fluorene |  |  |  |  |  |  |
| Chrysene |  |  |  |  |  |  |
| 1-Methylnaphthalene |  |  | .04(.03) | .85(.68) | .02(.03) | .43(.63) |
| 1-Fluoronaphthalene |  |  | .06(.05) | .84(.67) |  |  |
| 1-Chloronaphthalene |  |  | .30(.24) | .06(.05) | .16(.21) | .03(.04) |
| 1-Bromonaphthalene |  |  | .27(.22) | .002 | .14(.18) | .00 |
| 1-Iodonaphthalene |  |  | .38(.30) | .0005 | .20(.26) | .00 |
| 1-Hydroxynaphthalene |  |  | .04(.03) | .76(.61) |  |  |
| Quinoline |  |  | .19(.15) | .10(.08) | .10(.13) | .05(.07) |
| Benzophenone | .76(.61) | .00 |  |  | .74(.97) | .00 |
| Acetophenone | .63(.51) | .00 |  |  | .62(.82) | .00 |

a. A-Gilmore, Gibson, and McClure (11) in EPA at 77°K; "corrected" results.
B-Ermolaev and Svitashev (12) in EA (ether:alcohol 2:1) at 77°K relative to $\varphi_f$ for naphthalene taken as 0.55.
C-Ermolaev (15) in EA at 77°K relative to $\varphi_f$ for 9, 10-di-_n_-propylanthracene taken as 1.00.
D-Parker and Hatchard (18) in EPA at 77°K relative to $\varphi_f$ for fluorene taken as 0.54.
E-Lim(14) in EPA at 77°K using an integrating sphere.
F-Bowen and Williams (10) in hexane at room temperature.

TABLE I. Emission Quantum Yields (continued)

| Investigator:[a,d] | D | | E | | F | G | H |
|---|---|---|---|---|---|---|---|
| | $\varphi_p$ | $\varphi_f$ | $\varphi_p$ | $\varphi_f$ | $\varphi_f$ | $\varphi_f$ | $\varphi_p$ |
| Compound: | | | | | | | |
| Naphthalene | .01 | .39 | | | .38 | .11 | |
| Benzene | .19 | .21 | .20 | .20 | .11 | | |
| Triphenylene | .26 | .06 | | | | | .46 |
| Phenanthrene | .11 | .14 | | | .27 | .10 | .31 |
| Anthracene | | .21 | | | .46 | .29 | |
| Fluorene | .07 | [.54] | | | 1.02 | .54 | .13 |
| Chrysene | | | | | | | |
| 1-Methylnaphthalene | | | | | | | |
| 1-Fluoronaphthalene | | | | | | | |
| 1-Chloronaphthalene | | | | | | | |
| 1-Bromonaphthalene | | | | | | | |
| 1-Iodonaphthalene | | | | | | | |
| 1-Hydroxynaphthalene | | | | | | | |
| Quinoline | | | | | | | |
| Benzophenone | .71 | .00 | | | | | |
| Acetophenone | 1.00 | .00 | | | | | |

G-Weber and Teale (17) at room temperature in benzene, alcohol, or hexane.
H-Melhuish (19) in polymethylmethacrylate at 77°K.

b. Values in parentheses are reported values reduced by 20%.

c. Values in parentheses are reported values increased by 32%.

d. E and F used 2537 Å excitation, the others used excitation of wavelengths ≥ 3000 Å whenever possible.

"corrected" values are shown in Table I, along with some values reported by Ermolaev and Svitashev (12) for some naphthalene derivatives. The latter were measured relative to naphthalene fluorescence taken as 0.55, the value reported by Gilmore, Gibson, and McClure. In a more recent paper, Ermolaev (13) argued that the Gilmore, Gibson, and McClure values must be too large by 20-40%. This argument is supported by the fact that the most reliable values for the emission yields of benzene, those of Lim (14) measured using an integrating sphere, are 20% smaller than those measured by Gilmore, Gibson, and McClure. For purposes of comparison, Table I also lists the values of Gilmore, Gibson, and McClure, and those of Ermolaev and Svitashev reduced by 20%. Ermolaev (15) measured emission yields (in ether-alcohol at 77°K) relative to the fluorescence yield of 9,10-di-n-propylanthracene taken as 1.00, although the latter has been measured as 0.76 in fluid solution at room temperature (16). Therefore, listed (Table I) next to Ermolaev's reported values are values based on 0.76 as the fluorescence efficiency of 9,10-di-n-propylanthracene. Absolute fluorescence yields in solution were determined in a novel way by Weber and Teale (17). Parker and Hatchard (18) measured yields in EPA at 77°K using the Weber and Teale value for fluorene fluorescence as a basis. These results are listed in Table I along with the most recently reported phosphorescence yields measured for samples in polymethylmethacrylate at 77°K by Melhuish (19).

Almost all of the compounds listed in Table I exhibit total emission yields significantly smaller than unity. Thus, contrary to Kasha's original proposal, radiationless $S_1 \rightarrow S_0$ and/or $T_1 \rightarrow S_0$ transitions must be important. Before intersystem crossing efficiencies can be estimated from emission yields, some information about the relative importance of the radiationless $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ paths must be obtained. Contradictory opinions concerning the latter appear in the literature. Sveshnikov (20) supposed that both paths operate. Gilmore, Gibson, and McClure considered that radiationless $T_1 \rightarrow S_0$ deactivation alone accounted for the low total emission yields (11). Finally, Borgman et al. (21) concluded on the basis of measurements performed mainly on phthalimide derivatives, that radiationless deactivation occurs in the hypothetical intermediate state into which, according to them, the molecule falls before transition to the triplet state.

Invoking the rationale that the rate of radiationless combination varies inversely with the energy difference between the vibrationless levels of the two states involved, the view of Gilmore, Gibson, and McClure would seem reasonable. That is, intersystem crossing can compete with fast fluorescence while the radiationless $S_1 \rightarrow S_0$ transition cannot; however, radiationless $T_1 \rightarrow S_0$ deactivation can compete with slow phosphorescence. Support for this view was first supplied by triplet-triplet absorption spectroscopy. It is known that irradiation with flash or even ordinary lamps in the singlet-singlet absorption of many compounds leads to appreciable concentrations of molecules in the triplet state (22). On the other hand, many of the same compounds (anthracene, chlorophyll, and others) have a very small phosphorescence yield even in solid solution at low temperatures, so that the phosphorescence spectrum can be obtained only with great difficulty (23). However, the brilliant study by Ermolaev (15) of the quantum yields of sensitized phosphorescence in glassy solution at 77°K best supports the view that many organic molecules go with "great probability from the fluorescent to the triplet state but that even in solid solution at low temperatures the probability of transition from the triplet to the ground state without radiation is considerably greater than with radiation of phosphorescence." The method used was to compare measured sensitized phosphorescence yields with values calculated from the absolute quantum yields of ordinary fluorescence and phosphorescence of the donor and acceptor molecules assuming no radiationless $S_1 \rightarrow S_0$ deactivation. That is, he wished to determine whether the equality represented in equation 3 existed.

$$\left[\frac{\varphi_{p(\mathrm{Acceptor})}}{1-\varphi_{f(\mathrm{Acceptor})}}\right]\left[\frac{1-\varphi_{f(\mathrm{Donor})}}{\varphi_{p(\mathrm{Donor})}}\right]=\frac{\varphi_{\mathrm{sens.phos.(Acceptor)}}}{\varphi_{p(\mathrm{Donor})}-\varphi_{p}^{A}(\mathrm{Donor})}{}^{*} \qquad (3)$$

Satisfactory agreement (20-30% discrepancy) was obtained for fifteen donor-acceptor pairs. However, this technique does not yield absolute values for intersystem crossing yields nor does it yield absolute values for the fraction of triplets that phosphoresce. Too, the experimental uncertainty could hide a significant amount of radiationless $S_1 \rightarrow S_0$ deactivation.

## Emission Lifetimes

Both phosphorescent and fluorescent lifetimes can be measured with high accuracy by employing elegant electronic devices. These can be equated to the rates of the various processes as shown in equations 4 and 5, where $\tau_p$ and $\tau_f$ are the phosphorescent and fluorescent lifetimes, respectively, and $k_p$, $k_f$, $k_{ic}$,

$$1/\tau_p = k_p + k_{T_1 \rightarrow S_0} \qquad (4)$$

$$1/\tau_f = k_f + k_{ic} + k_{S_1 \rightarrow S_0} \qquad (5)$$

$k_{T_1 \rightarrow S_0}$, and $k_{S_1 \rightarrow S_0}$ are the rate constants for phosphorescence,

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* $\varphi_{p(\mathrm{Donor})}$ and $\varphi_{p}^{A}(\mathrm{Donor})$ are the yields of donor phosphorescence without and with acceptor present, respectively.

fluorescence, intersystem crossing, and radiationless $T_1 \rightarrow S_0$ and $S_1 \rightarrow S_0$ deactivation, respectively. Knowledge of the radiative lifetime for fluorescence ($\tau_f^o = 1/k_f$) and phosphorescence ($\tau_p^o = 1/k_p$) would yield information about the radiationless paths. Unfortunately, at best only order of magnitude calculations of $\tau_f^o$ and $\tau_p^o$ can be made from the relevant absorption spectra which for $S_0 \rightarrow T_1$ transitions are very difficult to obtain.

A very important and interesting effect is that of deuterium substitution on the phosphorescent lifetimes of aromatic hydrocarbons. This was first noticed by Hutchison and Magnum (24) for the case of naphthalene. Whereas naphthalene has a 2.1 sec phosphorescence lifetime in solid solution at low temperatures, naphthalene-$d_8$ exhibits a 16.9 sec lifetime. Kellogg (25) has measured the latter as 21 sec for samples in plastic films at 77°K. Wright, Frosch, and Robinson (26, 27) observed the same effect for benzene (7 sec) and benzene-$d_8$ (25.8 sec). Deuterium substitution reduces the radiationless $T_1 \rightarrow S_0$ rate significantly, and in these cases to the extent that the measured lifetimes are probably close to the true radiative lifetimes (14, 28). From these data, intersystem crossing in naphthalene is calculated to be 8 to 10 times the low temperature phosphorescence yield, and in benzene 3 to 4 times the phosphorescence yield. This technique, however, is probably very limited in application. It will be discussed again in later sections.

## Theories of Radiationless Transitions in the Solid Phase

In this section the two recently published theories of radiationless transitions will be briefly described. That of Gouterman (2) is based on a semiclassical model. "Radiationless transitions of a solute molecule embedded in a crystalline solvent are treated in close analogy to radiative transitions." A semiclassical interaction Hamiltonian couples solute particles to a force field amplitude set up by the phonons of the solvent.

Robinson and Frosch(3) perform a rigorous perturbation calculation based on a "simplified, but physically reasonable model; it is limited to those radiationless transitions which are slow compared with vibrational relaxation times, i.e. intersystem crossing, radiationless $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transitions especially. Electronic relaxation is treated as simply a result of radiationless transitions among nearly degenerate nonstationary states of the over-all system consisting of the solute molecule and the solvent. The final states nearly degenerate with the initial state consist of the final solute electronic state plus solute molecular vibrational additions plus solvent lattice vibrational additions. The radiationless transition can therefore occur by way of a time-independent perturbation to final states which are electronically nondegenerate with the initial state but which are degenerate with the initial state, or nearly so, when molecular and lattice vibrational additions to the final electronic state are included.

Although the two approaches give similar results, an important way in which they differ is in the emphasis given to lattice modes. While Gouterman puts strong emphasis on the importance of lattice vibrations, Robinson and Frosch stated that lattice vibrations will only slightly modify the pertinent perturbation terms which are already present in the free-molecule Hamiltonian. In the Robinson and Frosch model, the final states giving the largest contribution to the transition probability in complex molecules are generally those where the solute molecular vibrational energy greatly dominates the solvent lattice vibrational energy (these are called directly coupled states). The latter approach seems more satisfying for treating phenomena such as the deuterium substitution effect discussed in the previous section. Some conclusions based on the Robinson-Frosch treatment are discussed below.

The final result of the Robinson-Frosch treatment with regard to the radiationless transitions of interest here, internal conversion, intersystem crossing, and radiationless $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transitions, where in all cases there is a significant energy difference between the initial and final molecular electronic states, is given by equation 6, where $W$ is the transition probability, $t$ is the time, $\beta_{el}$ is the electronic matrix element connecting the initial

$$W(t)/t = (2\pi/\alpha\hbar) \sum_n \beta_n^{\,2} = (2\pi\beta_{el}^{\,2}/\alpha\hbar) \sum_n \langle\varphi_n''|\varphi_o'\rangle^2 \qquad (6)$$

and final states, $\alpha$ is the matrix element connecting states possessing lattice vibrational energy to each other and to the free solute state directly coupled to the initial state, and $\sum_n \langle\varphi_n''|\varphi_o\rangle^2$ is the over-all vibrational factor in the matrix element connecting the initial and the n directly coupled states. This equation applies for the limit $\Delta E >> \alpha >> \beta_n$, where $\Delta E$ is the electronic energy gap, and $\beta_n = \beta_{el}\langle\varphi_n''|\varphi_o'\rangle$.

The total vibrational overlap term in the Robinson-Frosch theory is simply the sum of Franck-Condon factors, the vibrational overlap in $\beta_n$. On the basis of these factors, the inverse relationship between $\Delta E$ and the rate of radiationless deactivation implied in Kasha's rule (4) is easily rationalized. That is, one considers vibrational overlap integrals between the vibrationless level of the initial state and high or low vibrational levels of the final electronic state. As $\Delta E$ increases, higher vibrational levels of the lower state become involved and the vibrational overlap integral becomes smaller. The importance of the Franck-Condon factors is seen in the deuterium substitution effect (27). The triplet state in benzene lies near 30000 cm$^{-1}$. The ground state vibrational quantum numbers corresponding to this energy are of the order of ten for C-H vibrations. Because of the lower amplitude of the C-D vibrations, much higher vibrational quantum numbers are required for the same electronic spacing, and smaller vibrational overlap integrals are obtained. Since the C-H vibrational mode is the most significant mode in the "tail" of the Franck-Condon envelope for benzene phosphorescence (29), deuterium substitution is expected to lead to a large decrease in the rate of the radiationless $T_1 \rightarrow S_0$ transition.

It is important to mention that Robinson and Frosch state (3) that their calculations cannot rule out the $S_1 \rightarrow S_0$ radiationless transition as being competitive with fluorescence and intersystem crossing. It is also important to notice that most workers in the field have neglected completely the possibility that reversible or irreversible photochemical reactions or the formation of unstable molecular complexes could present important pathways for deactivation (15).

For polyatomic solvents, the Robinson-Frosch treatment does not predict any specific solvent effects other than those arising from perturbation of $\beta_{el}$. Both the Gouterman and Robinson-Frosch theories predict no significant temperature effect. Neither theory can specifically deal with solvent viscosity effects, although from the emphasis on lattice modes one might expect viscosity effects to be important in the Gouterman theory. Estimations of the magnitude of temperature and viscosity effects are important in relating, for example, experimental data obtained at room temperature in liquid solution to that obtained at 77°K in solid solution. This point will be discussed at greater length in later sections.

Finally, some work has been reported on the calculation of the electronic matrix elements* (30, 31, 32). One area in which these calculations will be important is in determining the relative merits of the various paths for intersystem crossing, i.e. direct crossing from $S_1$ to $T_1$, or crossing from $S_1$ to a higher triplet followed by internal conversion. El-Sayed (31) has calculated matrix elements of the spin orbit operator between the various low-lying singlet and triplet states of some nitrogen heterocyclics and has decided that spin-orbit coupling between states of different configurations, i.e. $(S_{n\to\pi^*}, T_{\pi\to\pi^*})$ and $(S_{\pi\to\pi^*}, T_{n\to\pi^*})$ is larger than that between states of the same configuration $(S_{n\to\pi^*}, T_{n\to\pi^*})$ and $(S_{\pi\to\pi^*}, T_{\pi\to\pi^*})$. How the vibrational factors affect the over-all transition probabilities was not determined.

## The Importance of a Direct Determination of Intersystem Crossing

No doubt improvements in apparatus and new techniques will

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* The nature and forms of neither the electronic matrix elements connecting the various electronic states nor the interaction operators used in calculating them will be discussed in this work. A particularly good discussion of this topic is given by Robinson (32).

enable accurate (±5%) determinations of emission yields to be made in the near future. Emission lifetimes can already be measured with high accuracy. However, it is very doubtful that more than a few accurate true radiative lifetimes will be obtained by calculations, either semi-empirical molecular orbital calculations or semi-classical calculations based on absorption spectra, or experimentally by making use of special techniques such as deuterium substitution. Direct accurate determination of intersystem crossing would seem to be the best way to obtain information about all the processes, radiative and radiationless, occurring among the low-lying excited states of polyatomic molecules. From the intersystem crossing yield, and fluorescence and phosphorescence yields and lifetimes, rates for all the processes could be determined.

The remainder of this part describes a method for the determination of the intersystem crossing yield in fluid solution, lists the results for several compounds of interest, and contains a discussion of the results with respect to what has been presented in this introduction.

# THE EXPERIMENTAL METHOD AND RESULTS

## The Method in Principle:

A non-spectroscopic method for "counting" triplet excited molecules produced upon optical excitation of a substrate is, in principle, as follows. The system consists of the compound (sensitizer, S)* to be studied and a quencher (Q) possessing special properties. The electronic energy levels of the quencher must be disposed with regard to those of the sensitizer such that the lowest excited singlet state of the quencher lies much higher than the lowest excited singlet state of the sensitizer, while the lowest triplet state of the quencher lies below that of the sensitizer. This arrangement of excited states is shown schematically in Figure II. The scheme allows for optical excitation of the sensitizer without simultaneous excitation of the quencher. After formation of sensitizer triplets *via* intersystem crossing in the excited sensitizer molecules, triplet excitation transfer to the quencher producing quencher triplets will occur if a mechanism for transfer can operate under the experimental conditions. The quencher triplets must undergo some process leading to a detectable chemical change in

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* The compound being studied will be referred to as the *sensitizer* throughout this discussion.

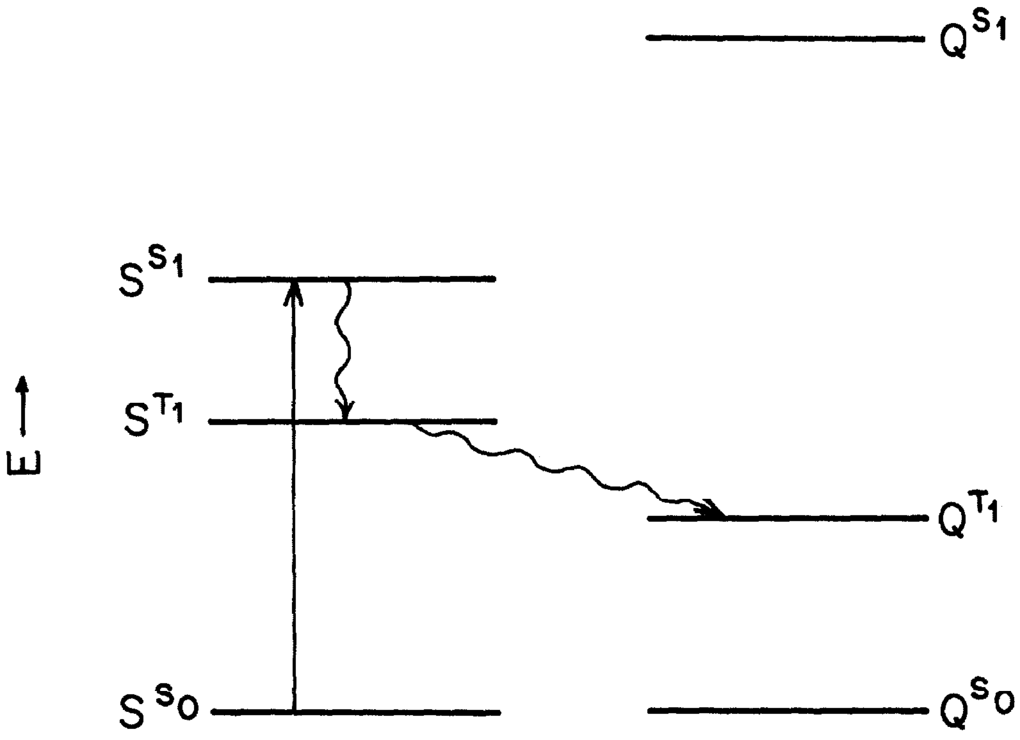

FIGURE II

the quencher molecules, that is formation of a product (P) by a rearrangement, fragmentation, dimerization, or reaction with an optically inert species also present. This scheme, represented by equations 6 to 9, is the "classical" one for triplet sensitized photo reactions (33).

$$S^{S_0} \xrightarrow{h\nu} S^{S_1} \qquad (6)$$

$$S^{S_1} \longrightarrow S^{T} \qquad (7)$$

$$S^{T} + Q^{S_0} \rightarrow S^{S_0} + Q^{T} \qquad (8)$$

$$Q^{T} \rightarrow P \qquad (9)$$

If the fraction of quencher triplets that undergo the reaction, equation 9, is known, and the fraction of sensitizer triplets quenched by Q, equation 8, is known, then by measuring the quantum yield of product (P), one can "count" the sensitizer triplets, that is, determine the fraction of excited sensitizer molecules which become triplets, equation 7. This scheme is simplified if conditions allow all of sensitizer triplets to be quenched by Q, equation 8.* These conditions are easily attainable in fluid solution and are discussed below.

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* Conservation of excited molecules is assumed in the quenching step, equation 8; that is, $S^T + Q \nrightarrow S^G + Q^G$. This matter will be discussed again later in this discussion.

## Intramolecular Energy Transfer in Fluid Solution:

Radiationless transfer of electronic excitation energy from the triplet state of a donor molecule leading to quenching of the donor and excitation of the acceptor molecule from its singlet ground state to its triplet state has been observed under a variety of conditions and has received much attention in recent years. The details of these studies may be found in two recent reviews (34, 35) and in the references contained in Part II of this dissertation. In general, the process requires close approach of the donor-acceptor pair, the mechanism probably involving exchange interaction due to overlap of electron clouds. In fluid solution, the close approach is achieved during collisions between the donor and acceptor. Various investigators (36, 37) have reported the same observations concerning the efficiency of the transfer process in fluid solution. The transfer is diffusion controlled (occurs with every collision between excited donor and ground acceptor) when the energy of the acceptor triplet is at least 2-4 kcal/mole lower than that of the donor. As the triplet energies become comparable, the transfer probability is reduced and no transfer is observed when the energy of the acceptor triplet is more than about 2 kcal/mole higher than that of the donor. This energy dependence is by far the controlling factor in the transfer probability. No dependence upon the probabilities of the ground singlet to triplet transitions in the donor or acceptor have been observed nor have any significant geometric (steric) effects been documented.

Using a sufficiently high concentration of acceptor which has a triplet level lower than the lowest triplet level of the donor, it is possible in fluid solution to guarantee quenching of all the donor triplets even if the latter have relatively short lifetimes. In benzene solution at room temperature, for example, the diffusion controlled bimolecular rate constant would be about $10^{10}$ ℓ/mole-sec. A $10^{-2}$ M concentration of suitable acceptor would quench 99% of the donor triplets if the latter had a $10^{-6}$ sec lifetime.

Another important characteristic of collisional exchange of excitation is the spin selection rule $X_{D*} + X_{A}' \rightarrow X_{D}' + X_{A*}$, where $X, X'$ are spin functions ($X'$ not necessarily equal to $X$). With regard to the scheme discussed here, it is particularly noted that no example of energy transfer from the lowest singlet level of the donor to a triplet level in the acceptor has been observed.

### The Quencher System; Photosensitized Isomerization of Olefins:

Recent investigations (38) of the mechanism of triplet photosensitized *cis*⇄*trans* isomerization of olefins have uncovered several olefins suitable as quenchers in a triplet counting scheme. In some cases, the details of the mechanism for isomerization have been worked out and direct application in triplet counting is straightforward. Some useful olefin pairs are: *cis*- and *trans*-piperylene (1,3-pentadiene), *cis*- and *trans*-stilbene, *cis*- and *trans*-$\alpha$-methylstilbene, and *cis*- and *trans*-$\beta$-methylstyrene. The essential features of these systems are discussed below.

The energies required for vertical[*] excitation of the olefins mentioned above from their ground states to their lowest excited singlet and lowest triplet states are given in Table II. The singlet level energies were extracted from absorption spectra of the compounds in ordinary solvents. The triplet level energies were obtained from absorption spectra of the compounds in perturbing environments, either a heavy atom-containing solvent (ethyl iodide) (40) or in the presence of high concentrations of molecular oxygen (39). Both of these environments cause an increase in the probability for multiplicity forbidden singlet to triplet transitions and allow detection of ground state to triplet level absorption.

As evident in Table II, the olefins listed possess relatively

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[*] These energies refer to that required to raise the compound from its ground state to a Franck-Condon excited state, that is the nuclei in the molecule do not move during the excitation process. Nonvertical processes such as those discussed by Hammond and Saltiel (45) play no part in the problem being discussed here, since it will be shown that situations where these processes might operate were avoided.

## TABLE II

Quencher Excitation Energies[a] (kcal/mole)

| Compound | Lowest Singlet $(S_0 \to S_1)$[b] | Lowest Triplet $(S_0 \to T)$ |
|---|---|---|
| *cis*-Piperylene | ~120 | 57.2[c], 56.9[d] |
| *trans*-Piperylene | ~120 | 58.8[d] |
| *cis*-Stilbene | ~ 92 | ~57[e] |
| *trans*-Stilbene | ~ 92 | 50.8[e], 49.5[f] |
| *cis*-α-Methylstilbene | ~ 92 | ~57[g] |
| *trans*-α-Methylstilbene | ~ 92 | ~50[g] |
| *cis*-β-Methylstyrene | ~ 95 | (>70)[h] |
| *trans*-β-Methylstyrene | ~ 95 | 59.8[d] |

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a. These values refer to the lowest energy absorption band observed in solutions of the compounds at room temperature. When band structure was not resolved, estimates were made based on the long wavelength tail of the absorption.

b. Estimated from absorption spectra in benzene or cyclohexane.

c. A 1M solution in ethyl iodide, 10 cm pathlength.

d. Oxygen perturbation technique in $CHCl_3$ (41).

e. Oxygen perturbation technique (42).

f. In ethyl iodide (43).

g. Estimated from data for the photosensitized isomerization (38) and from absorption spectra in ethyl iodide.

h. From data concerning the photosensitized isomerization (44).

large lowest excited singlet-lowest triplet splittings, one of the important requirements of the quencher in the triplet counting scheme. Most notable in this regard are the piperylenes, *trans*-stilbene, and *trans*-α-methylstyrene. A clearer picture of the applicability of these olefins is obtained by combining the triplet level data with the absorption characteristics of the olefins at the wavelengths of some of the useful mercury lines (Table III).

TABLE III

Absorption Characteristics of Quenchers

| Hg line(s) | 2537 Å | 3130 Å | 3340 & 3660 Å |
|---|---|---|---|
| Compound | | | |
| *cis*-Piperylene | $\epsilon = 8$ | no absorption[a] | no absorption |
| *trans*-Piperylene | $\epsilon = 32$ | " | " |
| *cis*-Stilbene | absorption[b] | absorption[b] | no absorption |
| *trans*-Stilbene | " | " | " |
| *cis*-α-Methylstilbene | " | " | " |
| *trans*-α-Methylstilbene | " | " | " |
| *cis*-β-Methylstyrene | " | no absorption | " |
| *trans*-β-Methylstyrene | " | " | " |

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a. $\epsilon < 1$

b. $\epsilon > 100$

These data show that *cis*-piperylene would be a suitable quencher for any substrate that strongly absorbs light of 2537 Å or longer wavelengths and which possesses a lowest triplet level that lies higher than 57 kcal/mole. At the other extreme, *trans*-stilbene and *trans*-$\alpha$-methylstilbene would be suitable quenchers for any substrate which absorbs light of 3340 Å or longer wavelengths and which possesses a lowest triplet level that lies higher than 50 kcal/mole. The other olefins listed are intermediate cases. As will be shown, these quenchers are useful for a large number of interesting substrates.

Although the complete description of the photosensitized isomerization of olefins as a function of sensitizer triplet excitation energy is complex, those features of the mechanism which apply when energy transfer from the sensitizer to the olefin does not involve non-vertical transitions (45) are completely understood and straightforward. The detailed mechanistic scheme given by Hammond (38) can be simplified for purposes of this discussion. This simple version is described by equations 10 to 15.

$$S^{S_0} \xrightarrow{h\nu} S^{S_1} \qquad (10)$$

$$S^{S_1} \xrightarrow{k_{ic}} S^{T_1} \qquad (11)$$

$$S^{T_1} + t \xrightarrow{k_1} S^{S_0} + T \qquad (12)$$

$$S^{T_1} + c \xrightarrow{k_2} S^{S_0} + T \qquad (13)$$

$$T \xrightarrow{k_3} t \qquad (14)$$

$$T \xrightarrow{k_4} c \tag{15}$$

Light is absorbed only by the sensitizer (S) exciting it to its first excited singlet state ($S^{S_1}$), equation 10. Formation of higher excited singlet states of the sensitizer by absorption at shorter wavelengths is followed by fast internal conversion processes leading to $S^{S_1}$. In general, excitation of substrates to states lying higher than the first excited singlet state were avoided in this study.* Some fraction of the excited singlet sensitizer molecules undergo intersystem crossing leading to formation of sensitizer molecules in their lowest triplet state ($S^{T_1}$), equation 11. Triplet energy transfer from $S^{T_1}$ to the <u>cis</u>- or <u>trans</u>-olefin results in vertical excitation of the latter to their planar spectroscopic triplet states. It is now assumed that very fast vibrational relaxation of both spectroscopic triplets obtains one triplet species of a different geometry or to a rapidly equilibrating system of triplet species, either case represented by T in the mechanistic scheme. Equations 12 and 13 combine the energy transfer step and the vibrational relaxation processes. Non-radiative decay from T leads back to the ground state olefins, equations 14 and 15. The details of the decay

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* Further discussion of possible complications due to formation of higher excited states is postponed to a later section.

process(es) are not known (38) except that in general both ground state isomers are obtained.

The useful kinetic expressions are easily derived from the mechanism given above if the concentration of the olefin triplet(s) [T] is treated by the steady-state assumption. The isomer ratio at photostationary state (p. s. s.) is given in equation 16.

$$\left(\frac{[c]}{[t]}\right)_{\text{p.s.s.}} = \left(\frac{k_1}{k_2}\right)\left(\frac{k_4}{k_3}\right) \qquad (16)$$

Two factors determine the photostationary-state composition, the triplet decay ratio $(k_4/k_3)$, which is independent of the sensitizer, and a factor dependent on the relative rates of excitation of the isomeric olefins. If the excitation energy of the sensitizer is sufficiently greater than that of either olefin isomer, energy transfer to both isomers will be diffusion-controlled $(k_1 = k_2)$. Under these conditions, the photostationary state ratio is determined only by the triplet decay ratio, equation 17. As long as sensitizer molecules do

$$\frac{[c]}{[t]}_{\text{p.s.s.}} = \frac{k_4}{k_3} \qquad (17)$$

not participate in the decay process, the value of $k_4/k_3$ should remain constant in any series of measurements made at constant temperature in a single solvent.

If all the sensitizer triplets transfer their excitation energy to olefin molecules, initial quantum yields ($\varphi$) for the interconversion of the olefin isomers are given in equations 18 and 19, where $\varphi_{ic}$ is the quantum yield of sensitizer triplets. The ratio of these quantum yields is the same as the photostationary state isomer ratio,

$$\varphi_{t\rightarrow c} = \varphi_{ic} \left( \frac{k_4}{k_3+k_4} \right) \tag{18}$$

$$\varphi_{c\rightarrow t} = \varphi_{ic} \left( \frac{k_3}{k_3+k_4} \right) \tag{19}$$

equation 20. The sum of these quantum yields gives the quantum

$$\frac{\varphi_{t\rightarrow c}}{\varphi_{c\rightarrow t}} = \left( \frac{k_4}{k_3} \right) = \left( \frac{[c]}{[t]} \right)_{p.s.s.} \tag{20}$$

yield for triplet formation for the sensitizer, equation 21. And

$$\varphi_{t\rightarrow c} + \varphi_{c\rightarrow t} = \varphi_{ic} \tag{21}$$

finally, the ratio of quantum yields for two sensitizers is the ratio of their triplet yields if all sensitizer triplets transfer excitation to olefin molecules, equations 22 and 23.

$$\frac{\varphi_{t\rightarrow c}\,(S_1)}{\varphi_{t\rightarrow c}\,(S_2)} = \frac{\varphi_{ic}\,(S_1)}{\varphi_{ic}\,(S_2)} \tag{22}$$

$$\frac{\varphi_{c\rightarrow t}(S_1)}{\varphi_{c\rightarrow t}(S_2)} = \frac{\varphi_{ic}(S_1)}{\varphi_{ic}(S_2)} \tag{23}$$

A scheme for quantitatively detecting triplet species in the gas phase by a similar quenching method has been suggested by Cundall (46). The cis ⇄ trans-isomerization of the 2-butenes was suggested as the triplet counting system. Since the details of isomerization in this system have not been worked out and the vertical excitation energies are high ($T_1 > 80$ kcal/mole (47)), this system can find only very limited application.

## Experimental Test of the Mechanism and Method--Benzophenone:

In this section the results of the experimental test of the triplet detecting scheme using benzophenone as the sensitizer are discussed. Experimental details are postponed to a later section.

Benzophenone was chosen as test sensitizer for several reasons. An intersystem crossing efficiency near unity was expected since no fluorescence and high yields of phosphorescence were reported for glassy solutions of benzophenone at 77°K (11, 15, 18). Quantum yield determinations for the photoreduction of benzophenone shown to proceed via the triplet state indicated unit efficiency for intersystem crossing (48). The lowest triplet of benzophenone lies 68.5 kcal/mole above its ground state (49). Diffusion-controlled energy transfer from triplet benzophenone to all the olefins listed in Table II, except cis-β-methylstyrene, is to be expected. Finally, benzophenone is photostable in non-hydrogen-donating solvents and exhibits a reasonable extinction coefficient at 3660 Å ($\epsilon$ = 63), where none of the olefins listed in Table III absorb.

The results* of the study using benzophenone as sensitizer are shown in Table IV. In the case of the α-methylstilbenes and the piperylenes, the ratios of the initial quantum yields for interconversion of the olefin isomers are equal to the photostationary isomer ratios as predicted in equation 20. The sum of the quantum yields in the two directions, which should equal the yield of benzophenone triplets, is 0.99±0.02 for both cis-trans pairs. In the case of the stilbenes, determination of the trans to cis quantum yield is complicated by quenching processes, including a bimolecular quenching process involving the trans-olefin (38, 50), equation 24. However,

$$T + t \rightarrow 2t \tag{24}$$

the intersystem crossing efficiency for benzophenone calculated from the cis to trans quantum yield and the photostationary isomer ratio for a range of olefin concentration is 0.99 ± 0.04. Quantum yield ratios calculated from the cis to trans quantum yield and assuming an intersystem crossing efficiency of 1.00 for

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* Details concerning this study have already been reported (38).

## TABLE IV

Quantum Yields for Benzophenone[b] Sensitized Isomerizations
(in benzene solution at 29-31°C; 3660 Å of excitation)

| Conc. Olefin | $\varphi_{t\to c}$ | $\varphi_{c\to t}$ | $(\varphi_{t\to c}/\varphi_{c\to t})$ | $([c]/[t])_{p.s.s.}$ | $\varphi_{t\to c}+\varphi_{c\to t}$ |
|---|---|---|---|---|---|
| α-Methylstilbenes[a] | | | | | |
| 0.05M | 0.55±.01 | 0.44±.01 | 1.25 | 1.24 | 0.99±.02 |
| Piperylenes[a] | | | | | |
| 0.05M | 0.44±.01 | 0.55±.01 | 0.80 | 0.81 | 0.99±.02 |
| *cis*-Stilbenes[a] | | | | | |
| 0.10M | --- | 0.37 | 1.70[c] | 1.50 | 0.93[d] |
| 0.05M | --- | 0.38 | 1.63[c] | 1.50 | 0.95[d] |
| | --- | 0.41 | 1.44[c] | " | 1.03[d] |
| 0.01M | --- | 0.39 | 1.56[c] | 1.50 | 0.98[d] |
| | --- | 0.41 | 1.44[c] | " | 1.03[d] |
| β-Methylstyrenes[e] | | | | | |
| 0.05M | 0.51 | 0.51 | 1.00 | 1.88 | 1.02 |

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a. Data of Hammond *et al.* (38).
b. Benzophenone concentration 0.05M in all cases.
c. Calculated from $\dfrac{1-\varphi_{c\to t}}{\varphi_{c\to t}}$.
d. Calculated from $\varphi_{c\to t} \times \left(\dfrac{[c]}{[t]}\right)_{p.s.s.}$.
e. Private communication from R. Steinmetz.
f. Light Source #1 (see *Experimental*).

benzophenone are also listed in Table IV. Quantum yield data for the β-methylstyrenes does not predict the photostationary isomer ratio using benzophenone as sensitizer. This is expected from the fact that energy transfer from benzophenone occurs at a diffusion-controlled rate to the *trans*-isomer but at a slower rate to the *cis*-isomer, i.e. $k_1 \neq k_2$ in equation 16. Consequently, the photostationary isomer ratio in this case is not the same as the decay ratio, $k_4/k_3$. However, the ratio of quantum yields at *low conversion* do reflect the decay ratio, since at the concentration of *cis*-olefin used, *all the benzophenone triplets will be quenched* by olefin molecules. Thus, the decay ratio for the β-methylstyrenes is predicted to be 1.00. Unfortunately, this prediction has not been tested since no sensitizer possessing sufficient triplet excitation which absorbs light at longer wavelengths than the β-methylstyrenes is available. Furthermore, the sum of the initial quantum yields in this case, 1.02, is a legitimate value for the efficiency of intersystem crossing for benzophenone.

These results with benzophenone are all consistent with the mechanism proposed for the photosensitized isomerization of the four olefin pairs for the case of high-energy sensitizers. The agreement between quantum yield measurements and photostationary state data is excellent. In the case of the piperylenes, this agreement was further tested with other sensitizers. These data are shown in Table V.

## TABLE V

### Quantum Yields in Isomerization of Piperylenes by High-Energy Sensitizers

| Sensitizer | Exciting Light, Å | $\varphi_{c\to t}$ | $\varphi_{t\to c}$ | $\varphi_{c\to t}/\varphi_{t\to c}$ |
|---|---|---|---|---|
| Benzophenone | 3660[b] | 0.55$\pm$.01 | 0.44$\pm$0.01 | 1.25 |
| Thioxanthone | 3130[c] | ---[d] | --- | 1.24 |
| Anthraquinone | 3130 | ---[d] | --- | 1.22 |
| Michler's ketone | 3130 | 0.55$\pm$.01 | 0.43$\pm$.01 | 1.23 |
| | | | Avg. | 1.24[a] |

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a. The value of $([t]/[c])_{p.s.s.}$ for high-energy sensitizers is 1.22$\pm$.05 (38).

b. Irradiation conditions 1; see Experimental.

c. Irradiation conditions 2.

d. Only relative quantum yields were measured.

The average value for $\varphi_{t\to c} + \varphi_{c\to t}$ from the data for all four olefin pairs listed in Table IV is 1.00$\pm$.03. Thus, intersystem crossing is completely efficient in benzophenone ($\varphi_{ic} = 1.00$), and every event involving transfer of excitation from benzophenone to an olefin molecule leads to an excited olefin capable of isomerization.

## Experimental Procedure:

A general description of the experimental procedure used in this study is given in this section. A detailed account is reported in the Experimental section.

Phillips research grade benzene was used as the solvent in all these determinations except in the determination of $\varphi_{ic}$ for benzene, where carefully purified trans-1,2-dimethylcyclohexane was used. The olefins were carefully purified by preparative gas chromatography and distillation or by repeated crystallization, and in the case of trans-stilbene, by zone refining. The olefins were all more than 99.6% isomerically pure, and with the exception of the piperylenes contained no impurities detectable by vapor phase chromatography (v.p.c.). The piperylenes contained small amounts (never more than 1%) of cyclopentene. The substrates (sensitizers) were purified by a variety of methods. Only naphthalene-$d_8$ was used as received from the manufacturer.

Carefully prepared samples contained in pyrex or quartz tubes were thoroughly degassed (freeze-pump-thaw method) and sealed under vacuum. All samples were stored in the dark when not in use. The samples contained enough sensitizer to absorb all the light of the wavelength to be used (in general, samples exhibited an optical density of 2-4 at the appropriate wavelength).

Medium pressure, high intensity mercury lamps in conjunction with Corning glass filters, interference filters, or a train of solution filters were used to obtain monochromatic exciting light of 3130 or 3660 Å wavelengths. A bank of low-pressure mercury lamps equipped with a solution filter was the source of radiation of 2537 Å wavelength. All the samples in a particular run received the same amount of radiation. This was accomplished in one of two ways. One method involved placing the samples in equivalent positions on a turntable which revolved around the light source. In the cases where the sample holder was stationary, the samples were interchanged periodically, so that each sample spent the same amount of time in each position of the cell holder. In all cases, irradiation was interrupted periodically and the contents of each sample tube mixed by shaking. This shaking, combined with the low conversions and long radiation times, precludes build-up of concentration gradients in the samples.

In the determinations of quantum yields using benzophenone as the sensitizer, potassium ferrioxalate actinometry (51) was employed. Actinometric samples were irradiated prior to, during, and at the end of each experiment, and the average value for the light intensity used. For determinations using other substrates, the actinometer was an identical sample, except that benzophenone was used as sensitizer. Since $\varphi_{ic} = 1.00$ for benzophenone, and from equations 22 and 23, *intersystem crossing yields could be determined by simply comparing conversions with conversions using benzophenone as sensitizer*, equation 25.

$$\varphi_{ic}(S) = \frac{\%\ \text{conversion}\ (S)}{\%\ \text{conversion}\ (\varphi_2CO)} \tag{25}$$

Irradiation times were adjusted so that conversions were 2-5% in most cases, although conversions as low as 1/2% and as high as 10% were obtained in some cases. All conversion data was corrected for blank and back reaction. Calculation of the correction, based on the mechanism proposed for the isomerization, is straightforward and an exact expression is obtained. The relationship between the corrected conversion B' and the observed conversion B is given by equation 26, where $\alpha$ is the fraction of the

$$B' = 2.303\,\alpha \log \left\{ \frac{\alpha}{\alpha - B} \right\} \tag{26}$$

isomer at photostationary state. All analyses were performed using the vapor phase chromatographic technique. Conversions of as little as 1/2% in a 0.05M solution of olefin were easily and accurately determined. Two samples with a particular sensitizer and two samples with benzophenone were employed for each determination. Each sample was analyzed twice.

## Results; Discussion of Accuracy:

The intersystem crossing efficiencies determined as described above are shown in Table VI. The benzophenone sensitized isomerization of the olefin under identical conditions served as the actinometer in all cases.

The effect of changing various experimental conditions was studied most intensely in the determination for naphthalene. Therefore, most of the discussion concerning the accuracy of the experimental method will employ naphthalene as a "test case."

The experimental method should be fairly insensitive to impurity quenching of sensitizer excited states. In the case of triplet sensitizer, this is guaranteed by the fact that quenching by olefin molecules overwhelms bimolecular quenching by oxygen or any minor impurity present in the sensitizer or olefin, since the concentration of olefin should be at least one-hundred times the concentration of any sensitizer or olefin impurity. However, a small per cent of quenching impurity in the solvent could compete with olefin for sensitizer triplets. It has already been shown that in the case of the benzophenone sensitized isomerization, the sum of the quantum yields for both directions is unity, precluding quenching of sensitizer triplets by solvent impurities. The relative efficiency for the benzophenone sensitized isomerization of cis-piperylene

# TABLE VI

## Intersystem Crossing Efficiencies

| Substrate | Conc(M) | Olefin[b] | Conc(M) | Excitation(Å) | Source[c] | $\varphi_{ic}$[d] | Comment |
|---|---|---|---|---|---|---|---|
| (Benzophenone) | | | | | | (1.00) | (see Table V ) |
| Naphthalene | .0125 | A | .05 | 3130 | 2 | 0.37) | naphthalene not |
| $E_T$[g] = 60.9 | | | | | | 0.36) | zone refined |
| | | | | | | 0.43 | |
| | | | | | | 0.40 | not totally degassed |
| | .025 | | | | | 0.40 | |
| | | | | | | 0.43 | |
| | .0075 | | | | | 0.36 | .03M benzophenone in actinometer |
| | .0125 | | .025 | | | 0.40 | |
| | | | .05 | | | 0.43 | |
| | | | .10 | | | 0.37 | |
| | | | .20 | | | 0.41 | |
| | | | .05 | 3130+3022 | 3 | 0.36 | |
| | | | | | 4 | 0.38 | |
| | | B | | 3130 | 2 | 0.41 | |
| | | | | | | 0.39 | |
| Naphthalene-$d_8$ | .0125 | A | .05 | 3130 | 2 | 0.39 | |
| | | | | | | 0.37 | |
| Naphthalene | .0125 | A | .05 | 3130 | 2 | 0.38 | cyclohexane solvent, |
| | | | | | | —— | actinometer had |
| | | | | | Avg. | 0.39±.02 | benzene solvent |

TABLE VI--2 (continued)

| Substrate | Conc(M) | Olefin[b] | Conc(M) | Excitation(Å) | Source[c] | $\varphi_{ic}$[d] | Comment |
|---|---|---|---|---|---|---|---|
| Triphenylene | .008 | A | .05 | 3130 | 2 | 1.06 | |
| $E_T = 66.6$ | | | | | | 0.95 | |
| | | | | | | 0.97 | |
| | | B | | | | 0.94 | |
| | | | | | | 0.89 | |
| | | | | | | 0.95 | |
| | | | | | | 0.87 | |
| | | | | | Avg. | 0.95±.05 | |
| Phenanthrene | .035 | A | .05 | 3130 | 2 | 0.75 | |
| $E_T = 62.2$ | | | | | | 0.74 | |
| | | B | | | | 0.77 | |
| | | | | | | 0.77 | |
| | | | | | Avg. | 0.76±.01 | |
| Chrysene | .01 | C | .05 | 3660 | 5 | 0.67 | |
| $E_T = 56.6$ | | | | | | | |
| 1,2,5,6-Dibenzanthracene | | | | | | | |
| $E_T = 52.3$ | .01 | C | .05 | 3660 | 5 | 0.89 | |
| Fluorene | .035 | A | .05 | 3130 | 2 | 0.32 | |
| $E_T = 67.6$ | | | | | | 0.32 | |
| | | B | | | | 0.32 | |
| | | | | | | 0.28 | |
| | | | | | Avg. | 0.31±.01 | |

TABLE VI--3 (continued)

| Substrate | Conc(M) | Olefin[b] | Conc(M) | Excitation(Å) | Source[c] | $\varphi_{ic}$[d] | Comment |
|---|---|---|---|---|---|---|---|
| Benzene[e] | .1 | A | .05 | 2537 | 6 | 0.22[f] | Naphthalene .004M |
| $E_T$ = 84.4 | .2 | | | | | 0.25[f] | " .004M |
| | .02 | | .01 | | | 0.24[f] | " .0008M |
| | | | | | Avg. | 0.24±.01 | |
| Diphenylamine | .01 | A | .05 | 3130 | 2 | 0.41 | |
| $E_T$ = 71.6 | | | | | | 0.35 | |
| | | | | | Avg. | 0.38±.03 | |
| Triphenylamine | .001 | A | .05 | 3130 | 2 | 0.83 | |
| $E_T$ = 70.1 | | | | | | 0.93 | |
| | | | | | Avg. | 0.88±.05 | |
| Carbazole | .002 | A | .05 | 3130 | 2 | 0.38 | |
| $E_T$ = 70.1 | | | | | | 0.34 | |
| | | | | | Avg. | 0.36±.02 | |
| Acetophenone<br>$E_T$ = 73.6 | 1.0 | B | .05 | 3660 | 1 | 0.99 | |
| p-Methylbenzophenone<br>$E_T$ = 68.5 | .05 | A | .05 | 3130 | 2 | 1.03 | |
| p-Bromobenzophenone<br>$E_T$ = 68.2 | .05 | A | .05 | 3130 | 2 | 1.01 | |

TABLE VI--4 (continued)

| Substrate | Conc(M) | Olefin[b] | Conc(M) | Excitation(Å) | Source[c] | $\varphi_{ic}$[d] | Comment |
|---|---|---|---|---|---|---|---|
| Michler's ketone | .01 | A | .05 | 3130 | 2 | 1.01 | |
| $E_T = 61.0$ | | | | | | | |
| 2-Acetonaphthone | .05 | C | .05 | 3660 | 5 | 0.84 | |
| $E_T = 59.3$ | | | | | | | |
| Fluorenone | .01 | C | .05 | 3660 | 5 | 0.93 | |
| $E_T = 53.3$ | | | | | | | |
| Benzil | .05 | C | .05 | 3660 | 5 | 0.92 | |
| $E_T = 53.7$ | | | | | | | |
| Anthraquinone | .01 | C | .05 | 3660 | 5 | 0.85 | |
| $E_T = 62.4$ | .001 | A | .05 | 3130 | 2 | 0.91 | |
| 1-Methylnaphthalene | | | | | | | |
| $E_T = 60.1$ | .0125 | A | .05 | 3130 | 2 | 0.46<br>0.49 | |
| | | | | | Avg. | $0.48 \pm .02$ | |
| 2-Methylnaphthalene | | | | | | | |
| $E_T = 59.5$ | .0125 | A | .05 | 3130 | 2 | 0.51<br>0.50 | |
| | | | | | Avg. | $0.51 \pm .005$ | |

TABLE VI--5 (continued)

| Substrate | Conc(M) | Olefin[b] | Conc(M) | Excitation(Å) | Source[c] | $\varphi_{ic}$[d] | Comment |
|---|---|---|---|---|---|---|---|
| Acenaphthene | .0125 | A | .05 | 3130 | 2 | 0.47 | |
| $E_T = 59.5$ | | | | | | 0.47 | |
| | | | | | Avg. | 0.47 | |
| 1-Fluoronaphthalene | | | | | | | |
| $E_T = 60.5$ | .0125 | A | .05 | 3130 | 2 | 0.63 | |
| | | | | | | 0.61 | |
| | | | | | | 0.64 | |
| | | | | | Avg. | 0.63 $\pm$ .01 | |
| 1-Naphthol | .0125 | A | .05 | 3130 | 2 | 0.29 | |
| $E_T = 58.9$ | | | .10 | | | 0.25 | |
| | | | | | | 0.28 | |
| | | | | | Avg. | 0.27 $\pm$ .02 | |
| 1-Methoxynaphthalene | | | | | | | |
| $E_T = 59.8$ | .0125 | A | .05 | 3130 | 2 | 0.24 | |
| | | | | | | 0.27 | |
| | | | | | Avg. | 0.26 $\pm$ .02 | |
| 1-Naphthylacetate | .0125 | A | .05 | 3130 | 2 | 0.31 | |
| $E_T = 58.3$ | | | | | | 0.26 | |
| | | | | | Avg. | 0.29 $\pm$ .03 | |

TABLE VI--6 (continued)

| Substrate | Conc(M) | Olefin[b] | Conc(M) | Excitation(Å) | Source[c] | $\varphi_{ic}$[d] | Comment |
|---|---|---|---|---|---|---|---|
| 1-Naphthoic Acid | .0125 | A | .05 | 3130 | 2 | 0.22 | |
| $E_T = 57.8$ | | | | | | 0.19 | |
| | | | | | Avg. | $0.20\pm.02$ | |
| 1-Naphthonitrile | .0125 | A | .05 | 3130 | 2 | 0.18 | |
| $E_T = 57.5$ | | | | | | 0.16 | |
| | | | | | Avg. | $0.17\pm.01$ | |
| 1-Naphthylamine | .0125 | A | .05 | 3130 | 2 | 0.14 | |
| $E_T = 57.5$ | | | | | | 0.15 | |
| | | | .10 | | | 0.15 | |
| | | | | | | 0.17 | |
| | | | | | Avg. | $0.15\pm.02$ | |
| Quinoline | .0125 | A | .05 | 3130 | 2 | 0.17 | |
| $E_T = 62.5$ | | | | | | 0.14 | |
| | | B | .05 | | | 0.16 | |
| | | | | | Avg. | $0.16\pm.02$ | |
| | | A | .05 | 3130 | 2 | 0.29 | dried benzene |
| | | | | | | 0.34 | |
| | | | | | Avg. | $0.32\pm.03$ | |

TABLE VI--7 (continued)

Footnotes:

a. Unless otherwise noted the solvent was Phillips Research Grade benzene and the actinometer was an identical solution except that benzophenone (.05M) was used as the sensitizer (substrate).

b. A = *cis*-piperylene, B = *trans*-β-methylstyrene, and C = *trans*-α-methylstilbene.

c. The code numbers refer to some combination of light source, filter system and irradiation apparatus as described in the *Experimental* section.

d. Corrected for blank, back reaction, and unabsorbed light when necessary.

e. 1, 2-*trans*-Dimethylcyclohexane was solvent. The actinometer was an identical solution except that naphthalene replaced the benzene.

f. Based on $\varphi_{ic} = 0.39$ for naphthalene.

g. $T_1 \rightarrow S_0$ in kcal/mole.

showed only a negligible change over an eight-fold variation of olefin concentration (Table VII). Thus, there is no significant amount of quenching impurity in the cis-piperylene. Oxygen quenching is precluded since even in one experiment using naphthalene as sensitizer in a sample which was only frozen, evacuated and sealed (no thaw cycles), the same intersystem crossing yield was measured as was measured for properly degassed samples. There was no difference in the intersystem crossing yield measured for naphthalene when the cis-piperylene concentration was varied from 0.025 to 0.2M or when the naphthalene concentration was varied from .0075 to .025M. The same yield was obtained when β-methylstyrene was the olefin used. Thus, no significant quenching of naphthalene excited states (singlet or triplet) was accomplished by impurities present in the naphthalene, cis-piperylene, or the β-methylstyrene.

None of the other sensitizers were purified to the extent that the naphthalene was purified (zone refining), although it is unlikely that they contained more than 1% of an impurity. This concentration level of impurity could not have competed with olefin for sensitizer triplets, but other modes of interference with the triplet "counting" scheme can be envisoned. If the impurity quenched sensitizer singlets at the diffusion-controlled rate, significant quenching of long-lived sensitizer singlets might occur. For example, if the impurity were 1% and the sensitizer concentration

## TABLE VII

### Relative Efficiencies of the Benzophenone[a] Sensitized Isomerization of *cis*-Piperylene at Various Olefin Concentrations

| Concentration of *cis*-Piperylene(M) | Relative Isomerization Efficiency |
|---|---|
| 0.025 | 0.99 |
| 0.05 | 1.00 |
| 0.10 | 1.00 |
| 0.20 | 1.01 |

a. $[\varphi_2CO] = .05M$.

.025M, 20% of the sensitizer singlets which have a $10^{-7}$ sec lifetime would be quenched for a bimolecular quenching constant of $10^{10}\ \ell\, M^{-1} sec^{-1}$. Although the latter represents an extreme case, it does point out that the highest sensitizer purity is certainly desirable, especially since other mechanisms such as dipole-dipole resonance transfer (52) of singlet excitation does not even require collision of donor and acceptor. In cases where purity is questionable, measurements of the intersystem crossing yields at various sensitizer concentrations would tell whether the impurity were quenching excited singlet sensitizer molecules. Unfortunately, this kind of data is only available for the naphthalene case. Another way in which an impurity could interfere is by competing with the sensitizer for the exciting light. This is especially serious if the impurity is a much stronger absorber of the excitation. Take the example of "reagent grade" phenanthrene which contains about 1% anthracene. At 3130 Å, the anthracene impurity would absorb 10% of the light.

Self-absorption of sensitizer fluorescence leads to a fictitiously high intersystem crossing yield. At the sensitizer concentrations employed in these measurements, some reabsorption of sensitizer fluorescence cannot be avoided. However, in most cases the overlap between the fluorescence and absorption spectra is small and probably not more than about 10% of the fluorescence is reabsorbed. For a sensitizer that has $\varphi_f = 0.5$ and $\varphi_{ic} = 0.5$, reabsorption of 10% of the fluorescence would give a 4% error in the intersystem crossing yield. Thus, in most cases, reabsorption of fluorescence is a minor problem.

Excimer (excited singlet dimer) (53) formation is another way in which singlet excitation could be "abnormally" degraded. That is, radiationless decay of the excimer to the ground state monomers, to some short-lived "chemical" dimer, or to a triplet monomer and a ground state monomer, could take place and proceed at relative efficiencies different than in excited singlet monomer. These relative efficiencies are not known for any excimer system. A decay path leading to a stable "chemical" dimer has been demonstrated in the case of anthracene (54) and other polyacenes (55), and recently for a substituted naphthalene (56). But the yields of these dimers are small. Furthermore, in the case of naphthalene (57) and probably for most organic systems, at the conditions of concentration and temperature employed in the determination of the intersystem crossing yields, excimer formation is not very important. Besides, the constancy of the intersystem crossing yield for naphthalene over a three-fold concentration range precludes interactions involving ground state naphthalene. Concentration dependence studies for the other sensitizers would yield definitive information about complications due to excimer formation, etc. for these systems. These studies should be carried out.

The effects of impurity quenching on the olefin isomerization should be negligible. The photosensitized isomerization of the stilbenes is the only isomerization known to change significantly due to quenching of olefin triplets by low energy quenchers (38). This is why stilbene was not used in these determinations. None of the other olefin systems used, including the $\alpha$-methylstilbenes, exhibit significant impurity quenching effects.

The triplet state energies of some of the naphthalene derivatives studied are close to the triplet state energy of the olefin used, cis-piperylene. However, for two of these derivatives, the intersystem crossing yields measured using 0.1M olefin were the same as those measured using 0.05M olefin. Thus, 0.05M cis-piperylene is sufficient to quench the triplets of all the naphthalene derivatives studied totally.

Only in the case of quinoline was the benzene solvent dried. This led to an increase in the measured intersystem crossing yield. A discussion of this result will be found in later sections.

The determination of triplet formation efficiency in excited benzene needs special comment. The olefin chosen was, of course, cis-piperylene. The solvent was trans-1, 2-dimethylcyclohexane. This choice was made for purposes of good vapor phase chromatographic determination of the piperylenes. All of the other saturated hydrocarbons examined for use as solvent interfered with the analysis. The trans-1, 2-dimethylcyclohexane was Phillips Pure Grade and was further purified until a one-centimeter path showed an optical density of less than 0.05 at 2537 Å. The actinometers in this case were similar solutions, except that naphthalene replaced the benzene. Benzophenone could not be used as actinometer sensitizer because triplet benzophenone abstracts hydrogen atoms from saturated hydrocarbon solvents with fair efficiency (48, 58). Naphthalene was chosen as actinometer-sensitizer because among the hydrocarbons its intersystem crossing yield was most carefully determined. The only objection in this application is that the triplet yield for naphthalene may be different in trans-1, 2-dimethylcyclohexane with 2537 Å excitation than in benzene with 3130 Å excitation. Although there is some evidence that excitation to higher singlet states could lead to an increase in triplet yield even in the condensed phase (59), there is no evidence that a large increase could be expected here. In all the samples and actinometer samples, the cis-piperylene absorbed 2-4% of the light. No correction was made for this. This brings up the point that since the lowest singlet states of benzene and cis-piperylene lie close to each other, and since the lowest singlet state of benzene is relatively long-lived, some transfer of singlet excitation from benzene to cis-piperylene might be expected. That this is not occurring is evidence by the fact that although the photoisomerization of the piperylenes achieved by direct excitation (presumably little or no intersystem crossing occurs in piperylene) exhibits a very large (~ 10) trans/cis decay ratio (60), irradiation of piperylene in benzene with 2537 Å light gives rise to the photostationary state characteristic of the triplet pathway (t/c = 1.25) (58). Furthermore, although one might expect a competition between intersystem crossing and transfer of benzene singlet excitations to the piperylene, the measured benzene triplet yield (0.24±.01) was the same for 0.01 to 0.05M cis-piperylene. No excited benzene-ground state benzene interactions seem to be important, since the same triplet yield was measured over a ten-fold variation in benzene concentration.

The precision in these determinations is good (±5%) and there is no reason to believe that the accuracy cannot be at least ±10%. Extensive purification and enlarged studies of concentration effects for all the sensitizers, as was done for naphthalene, would put all the intersystem crossing yields on a very firm basis.

# DISCUSSION

The purpose of the following discussion will be twofold. Presently available experimental data and current theories will be examined to determine to what extent the intersystem crossing data obtained in this work can be compared to various data obtained under vastly different experimental conditions, namely from samples in solid solutions at very low temperatures. In light of this, the data obtained in this work will be compared with various data extracted from the literature in attempts to estimate the importance of radiationless $S_1 \rightarrow S_0$ transitions, to estimate rates for some radiationless transitions, to estimate some $T_1 \rightarrow S_0$ true radiative lifetimes, and to uncover any significant discrepancies which might require modification of current ideas about deactivation processes. Some suggestions for future work will be made.

## Temperature Effects on Radiationless Transitions

Some discussion of the effect of temperature changes in the rate of radiationless transitions was given in the Introduction. It was pointed out that neither of the two current theories (2, 3) of radiationless transitions predicted a significant temperature effect for molecules in a polyatomic solvent where the density of final solvent states is large. However, it was also pointed out that experimental data in this regard is scarce. Too, most of the data is concerned with phosphorescence lifetimes.

Lewis, Lipkin, and Magel (61) first studied the temperature effect on a phosphorescence lifetime. They reported that the phosphorescence lifetime of fluorescein in boric acid glass is the same at 77°K as it is at 20°K. The most extensive data of this type are those for naphthalene phosphorescence. Robinson and Frosch reported (3) that naphthalene in EPA glass exhibits the same phosphorescence lifetime at 4.2°K as at 77°K. The phosphorescence lifetime for naphthalene in solid polymethylmethacrylate changes from 2.2 sec at 77°K to 1.2 sec at room temperature (62). Naphthalene-$d_8$ under the same conditions gives 21 sec at 77°K and 16 sec at room temperature (41). Hadley, Rast, and Keller (63) reported that the phosphorescence lifetimes of naphthalene and naphthalene-$d_8$ in durene crystal did not change over the range 77-200°K. The fast drop-off in the lifetimes they observed above 200°K was probably due to oxygen quenching, the diffusion of oxygen through the crystal being an activated process. Hadley <u>et al</u>. also reported that within experimental error (10%), there was no change in the intensity of fluorescence from the two samples from 77°K to room temperature. The phosphorescence lifetime of triphenylene in plastic films changes from 16 sec at 77°K to 9.4 sec at room temperature (41). On the other hand, significant variations in the fluorescence yields with temperature have been observed for a number of anthracene and stilbene derivatives.

The most extensive data on the temperature dependence of fluorescence yields are those of Bowen (64, 65, 66) for anthracene and anthracene derivatives in fluid solution. He reported heats of activation for fluorescence degradation as large as 10 kcal/mole. However, for the compounds exhibiting large activation energies, these correspond fairly closely to the "activation energies" for the solvent viscosity. The more rigid anthracene derivatives show the smaller activation energies for fluorescence degradation. Some more discussion of these data will be found in the next section.

The intensity of fluorescence from _trans_-stilbene increases twelve-fold on going from room temperature to 90°K (67, 68). Malkin and Fischer interpreted these results along with those from a study of the _cis_⇄_trans_ photoisomerization of _trans_-stilbene in terms of an activated formation of a hypothetical singlet state from which intersystem crossing takes place much more efficiently than from the fluorescent state. _cis_-Stilbene shows a weak fluorescence at 77°K which disappears at room temperature (69). These results were interpreted in terms of an activated process leading to formation, from the fluorescent state, of an unstable photoproduct. There are undoubtedly many more examples of isomerization reactions of electronically excited molecules which proceed through activated processes. This kind of behavior has not been considered in the theoretical treatments of radiationless transitions.

At the present state of the art, it is almost impossible to predict for certain whether a molecule will undergo some sort of temperature dependent isomerization while in its lowest excited electronic states. Thus, in comparing *vide infra*, the intersystem crossing yields obtained in this study with low temperature emission yields, it must be kept in mind that discrepancies may be due not only to radiationless $S_1 \rightarrow S_0$ transitions (which may or may not be temperature dependent) in the direct sense, but also to decay paths for $S_1$ which involve the formation of high energy isomers which may or may not be temperature dependent.

## Viscosity Effects on Radiationless Transitions

Solvent viscosity plays an important role in radiationless transitions involving bimolecular quenching mechanisms. But in the determinations of intersystem crossing yields carried out in this work, viscosity dependent quenching by chemical impurities was shown to be negligible. However, other viscosity dependent effects on radiationless transitions can be envisioned. These effects would be temperature dependent since the viscosity is temperature dependent.

Robinson and Frosch (3) envision a radiationless mechanism involving quenching by physical defects qualitatively described on the basis of large solvent perturbations on the molecular potential-energy surfaces. An increase in the magnitude of the vibrational factors could then result. They state that this would be expected to be most serious in the liquid state where the structure is primarily defect structure. Large time-dependent perturbations caused by local density fluctuations may increase the probability for transition relative to that in the solid. Gouterman (2) also alludes to the possibility of an increase in the radiationless transition probability due to the introduction of higher energy lattice modes with an increase in temperature.

Extensive measurements of triplet state lifetimes in fluid solution have been made by the flash photolytic technique (70, 71). The solution lifetimes are so very short ($10^{-3}$-$10^{-5}$ sec) that phosphorescence under these conditions is precluded. The decay processes which lead to these short lifetimes are still only partly understood. At low light intensities (low triplet concentrations) where triplet-triplet interaction (70) is negligible, the contributing processes are true unimolecular conversions to the ground state, both radiative and radiationless as well as pseudo-first-order processes involving a quenching molecule which may be oxygen or some other adventitious impurity (70). In fluid solvents near room temperature, the first-order triplet decay constant is usually strongly dependent on solvent viscosity, and this is now thought to be due to the fact that pseudo-first-order quenching processes predominate under these conditions (74). This view is supported by the fact that the viscosity dependence of decay rate can be greatly reduced by increasing the rate of the spontaneous process (e.g. by heavy atom substitution) or the use of very pure solvents (71, 72, 73). Most important is the recent study by Porter (74) of triplet decay rates in two solvent systems over a viscosity range varying by a factor of $10^8$. When allowance was made for discontinuities in the viscosity-temperature relations, all of the data could be accounted for in terms of two regimes of triplet decay: a high viscosity regime where the rate is nearly independent of temperature and viscosity and the mechanism is truly unimolecular, and a low viscosity regime where diffusion-controlled quenching (probably mostly by residual oxygen) processes are operative. In the high viscosity regime, the small change in the decay rates with temperature were attributed to a slight temperature dependence and not an effect of the nature of the solvent or the viscosity. For naphthalene in isopentane the triplet lifetime was found to be 3.3 sec at 77°K and the extrapolated value (extrapolation of the high viscosity regime data) for 20°C was reported to be 2.5 sec.

As mentioned in the previous section, the fluorescence yields from anthracene and anthracene derivatives (64, 65, 66) decrease with increasing temperature and show significant activation energies, and that for the "flexible" derivatives these were large (~ 10 kcal/mole) and probably associated with the solvent viscosity. For the more rigid derivatives, the activation energies were very much smaller (0-1 kcal/mole), but still seem in part to be due to the temperature dependence of the solvent viscosity. The Arrhenius plots do not show any breaking points, as was found by Porter (74) in his triplet lifetime study. But the temperature range covered was only +50 to -50°C. Due to the shortness of the fluorescence lifetimes, diffusion-controlled bimolecular quenching by adventitious impurities probably cannot account for this viscosity dependence. However, this point has not been examined in great detail. Certainly the interpretation of these data is far from clear, and only by great improvement in experimental precision and extension of the study to other systems can this subject be taken further.

A comparision of the intersystem crossing data obtained in this study with respect to low temperature emission yields and other available data follows. Although the importance and nature of the temperature and viscosity dependences of the various processes are not known at this time, a comparison of the available data is still valuable, since discrepancies noted in this comparison would probably point out where these effects do operate. For purposes of discussion, it will be assumed that in most cases the rate of intersystem crossing is not significantly temperature or viscosity dependent. That is, in the absence of temperature or viscosity effects on other decay paths of $S_1$, the intersystem crossing yields obtained in this study represent upper limits to what would be obtained in glassy solution at 77°K.

## The Aromatic Hydrocarbons

With the exception of the data for benzene, the intersystem crossing yields obtained for the aromatic hydrocarbons fit in fairly well with their measured low-temperature emission yields.

Table VIII shows values of $1-(\varphi_f + \varphi_{ic})$ for five of the hydrocarbons for which fluorescence yield data is available. The emission yields used in this discussion are taken from Table I. The modified ("corrected" to the prejudice of this author) values are used if there is a choice.

For naphthalene, $1-(\varphi_f + \varphi_{ic})$ is 0.17 - 0.23, using four low-temperature $\varphi_f$ values. The room temperature $\varphi_f$ values listed are quite different. That of Bowen and Williams (0.38) agrees exactly with the low temperature values. However, most of the Bowen and Williams values seem too high. That of Weber and Teale (0.11)

## TABLE VIII

### Estimation of Some Radiationless $S_1 \to S_0$ Efficiencies

| Compound | $\varphi_{ic}$[a] | $1-(\varphi_f + \varphi_{ic})$[b] | | | | | |
|---|---|---|---|---|---|---|---|
| | | A[b] | B | C | D | F | G |
| Naphthalene | 0.39 | 0.17 | [0.17] | 0.23 | 0.22 | 0.23 | 0.50 |
| Triphenylene | 0.95 | 0.01 | --- | --- | 0.0 | --- | --- |
| Phenanthrene | 0.76 | --- | --- | 0.08 | 0.10 | 0.09[c] | 0.14 |
| Fluorene | 0.31 | --- | --- | --- | [0.15] | (-0.30) | 0.15 |
| 1-Methylnaphthalene | 0.48 | --- | (-0.16) | (-0.11) | --- | --- | --- |

---

a. $\varphi_{ic}$ values are from Table

b. $\varphi_f$ values are from Table I. The code letters for the various investigators correspond to those in Table I.

c. Calculated from $\varphi_f = 0.15$ in ligroin at room temperature (66).

gives a $1-(\varphi_f + \varphi_{ic})$ value of 0.50. Barker et al. (75) report 0.19 for $\varphi_f$ in ethanol at room temperature, giving $1-(\varphi_f + \varphi_{ic}) = 0.42$. At the same time, the intensity of fluorescence from naphthalene in durene crystal is reported to be constant from 77°K to room temperature (76). Parker (57) reported that from a kinetic analysis of the delayed fluorescence of naphthalene in solution, the intersystem crossing yield must be temperature independent over the range -77 to +22°C. (Parker's estimate of $\varphi_{ic}$ in solution is 0.52.) From the $1-(\varphi_f + \varphi_{ic})$ data at room temperature, there is no doubt that another deactivation path(s) for $S_1$ is operating besides fluorescence and intersystem crossing. It is probably unwise to conclude the same for naphthalene at low temperatures in glassy solution until more accurate emission data are available and temperature and viscosity effects are known.

In the case of triphenylene, the low temperature fluorescence yield (0.05) plus the room temperature intersystem crossing yield (0.95) gives unity. Triphenylene also fluoresces at room temperature in solution, although the yield has not been measured. One can probably safely conclude that for triphenylene in its $S_1$ state, fluorescence and intersystem crossing are the only deactivation paths that operate at 77°K or at room temperature.

In the case of phenanthrene, the room temperature and low temperature fluorescence yields agree quite well. Calculated values for $1-(\varphi_f + \varphi_{ic})$ range from 0.08 to 0.14, which may be attributable to radiationless $S_1 \rightarrow S_0$ decay or may reflect experimental uncertainty. Bowen and Williams' value for the fluorescence yield for fluorene is obviously in error. The value given by Weber and Teale also for solution at room temperature gives 0.15 for $1-(\varphi_f + \varphi_{ic})$ for fluorene. Both low temperature fluorescence yields reported for 1-methylnaphthalene lead to negative $1-(\varphi_f + \varphi_{ic})$ values, -0.16 and -0.11, which indicates that intersystem crossing better competes with fluorescence at high temperatures in this system, or again merely reflects experimental uncertainty.

Estimates of true $T_1 \rightarrow S_0$ radiative lifetimes $\tau_p^{\,o}$ and radiationless $T_1 \rightarrow S_0$ transition rates are listed in Tables IX and X. Low temperature phosphorescence yields, the room temperature intersystem crossing yields, and the low temperature triplet (phosphorescence) lifetimes reported by McClure (77) were used to obtain these estimates.

Naphthalene-$d_8$ exhibits a 21 sec phosphorescence lifetime in plastic films at low temperature (41). This is probably close to the true radiative lifetime (28). The phosphorescence yields reported by Ermolaev lead to a 23 sec calculated true radiative lifetime for naphthalene. The phosphorescence lifetime of perdeuterotriphenylene

## TABLE IX

### Estimated True $T_1 \rightarrow S_0$ Radiative Lifetimes $\tau_p^o$

| Compound | $\tau_p$[a](sec) | $\tau_p^o$[b] (sec) | | | | |
|---|---|---|---|---|---|---|
| | | A | B | C | D | H |
| Naphthalene | 2.3 | 12 | 23 | 23 | 90 | --- |
| Triphenylene | 15.9 | 36 | --- | --- | 58 | 33 |
| Phenanthrene | 3.3 | --- | --- | 14 | 23 | 8 |
| Chrysene | 2.6 | --- | --- | --- | --- | 13 |
| Fluorene | 4.9 | --- | --- | --- | 22 | --- |
| 1-Methylnaphthalene | 2.1 | --- | 34 | 34 | --- | --- |
| Benzophenone | 0.006 | 0.01 | --- | 0.006 | --- | 0.009 |
| Acetophenone | 0.008 | 0.016 | --- | 0.01 | --- | 0.008 |

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a. Lifetime data of D. S. McClure (77) for samples in EPA at 77°K.

b. Calculated from $\frac{\varphi_{ic}}{\varphi_p} \times \tau_p$. The phosphorescence yields are taken from Table I. The code letters for the various investigators correspond to those in Table I.

# TABLE X

## Estimated Radiationless $T_1 \rightarrow S_0$ Transition Rates

| Compound | $E_{T_1}$ (cm$^{-1}$)$^b$ | $k^{-1}_{T_1 \rightarrow S_0}$ (sec)$^a$ | | | | |
|---|---|---|---|---|---|---|
| | | A | B | C | D | H |
| Chrysene | 19800 | --- | --- | --- | --- | 3.3 |
| 1-Methylnaphthalene | 21000 | --- | 2.2 | 2.2 | --- | --- |
| Naphthalene | 21300 | 2.9 | 2.6 | 2.6 | 2.4 | --- |
| Phenanthrene | 21600 | --- | --- | 4.3 | 3.8 | 5.7 |
| Triphenylene | 23500 | 29 | --- | --- | 22 | 31 |
| Fluorene | 23800 | --- | --- | --- | 6.3 | --- |
| Benzene | 29600 | (9)$^c$ | | | | |
| Benzophenone | 23950 | 0.015 | --- | >0.06 | --- | 0.018 |
| Acetophenone | 25700 | 0.016 | --- | 0.04 | --- | >0.08 |

---

a. Calculated from $k_{T_1 \rightarrow S_0} + 1/\tau_p^o = 1/\tau_p$.
$\tau_p$ and $\tau_p^o$ values are taken from Table IX.

b. Approximate $T_1 \rightarrow S_0$ O'-O band energy.

c. Calculated from $\tau_p = 7$ sec (EPA at 77°K) and $\tau_p^o = 28$ sec (14).

in plastic films at 77°K is 21 sec (41). The calculated true radiative lifetime given in Table IX is 33-58 sec. So that in the case of triphenylene, whose triplet lies higher than that of naphthalene, perdeuteration does not obtain the true radiative $T_1 \rightarrow S_0$ lifetime.

As expected from the fact that the phosphorescence yields for all of the hydrocarbons listed in Table X, except for triphenylene, are low, the radiationless $T_1 \rightarrow S_0$ lifetimes ($k^{-1}_{T_1 \rightarrow S_0}$) are close to the phosphorescence lifetimes. The hydrocarbons in Table X are listed in order of increasing $T_1 \rightarrow S_0$ energy gap. A calculated value for benzene is included. This is based on data of Lim (14) and Robinson et al. (26), and is probably corrected, vide infra. The radiationless $T_1 \rightarrow S_0$ lifetimes show definite increase with increasing triplet energy except that triphenylene seems way out of line. A rationale for the anomalous behavior of triphenylene is that different vibrational modes are important for triphenylene than for the other hydrocarbons listed and that the Franck-Condon factors for these modes are small. It might be that in all the other hydrocarbons listed, C-H modes are most important. In triphenylene, the "excitation" could be "localized" at the center of the molecule, reducing the importance of C-H vibrations. This would also explain the relatively small change in phosphorescence lifetime on perdeuteration of triphenylene. This rationale assumes, of course, that the electronic term connecting the $T_1$ and $S_0$ states is nearly the same for all the aromatic hydrocarbons considered.

Table XI shows an attempt to determine the relative rates of intersystem crossing $(k_{ic})$ for some of the aromatic hydrocarbons. The intersystem crossing yields, of course, do not reflect the intersystem crossing rates. To estimate the rates one can assume that the only competing process is fluorescence. Then the intersystem crossing rate is given by equation 27,

$$k_{ic} = \left(\frac{\varphi_{ic}}{1 - \varphi_{ic}}\right) k_f \tag{27}$$

where $k_f$ is the fluorescence rate. The oscillator strength f is a quantity which is proportional to the fluorescence rate (78) and so relative intersystem crossing rates can be obtained if f values are known. Oscillator strengths can be calculated from absorption spectra (78), but very few have been reported in the literature. Those reported by McClure (76) are listed in Table XI, and relative intersystem crossing rates calculated using these values are shown. Rough estimates from absorption spectra give $f_{S_1 \rightarrow S_0}$ values near 0.05 for fluorene and 0.01 for 1,2,5,6-dibenzanthracene and relative $k_{ic}$ values of 0.023 and 0.08, respectively.

Kasha (9) has pointed out that the intersystem crossing ratio falls off rapidly in the series triphenylene, phenanthrene, chrysene,

# TABLE XI

Relative Intersystem Crossing Rates in Aromatic Hydrocarbons

| Compound | $\Delta E^{a}_{S_1 \rightarrow T_1}$ (cm$^{-1}$) | $\varphi_{ic}$ | $f_{S_1 \rightarrow S_0}$ | rel. $k_{ic}$ [c] |
|---|---|---|---|---|
| Naphthalene | 10,500 | 0.39 | 0.002[b] | 0.0013 |
| Fluorene | 9,450 | 0.31 | 0.05[d] | 0.023 |
| Chrysene | 7,700 | 0.67 | 0.005[b] | 0.01 |
| 1,2,5,6-Dibenzanthracene | 7,000 | 0.89 | 0.01[d] | 0.08 |
| Phenanthrene | 6,700 | 0.76 | 0.003[b] | 0.009 |
| Triphenylene | 5,400 | 0.95 | 0.012[b] | 0.23 |

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a. Difference between the O'-O fluorescence band and the O'-O phosphorescence band measured in EPA at 77°K.

b. These are oscillator strengths reported by McClure (77).

c. Calculated from $k_{ic} = f\left(\frac{\varphi_{ic}}{1-\varphi_{ic}}\right)$.

d. Estimated from room temperature absorption spectra using $f = 4.3 \times 10^{-9} \int \varepsilon d\nu$.

naphthalene, while the $S_1$-$T_1$ energy gap increases: 5400 , 6700, 7700, and 10,700 $\mathrm{cm}^{-1}$, respectively. Kasha claims this supports the idea that intersystem crossing, like internal conversion, is easier the closer the two states involved. However, various calculations of the triplet levels in alternate aromatic hydrocarbons (79, 80, 81) predict that a low-lying singlet state ($^1L_b$) is always degenerate with a triplet state ($^3L_b$) which lies higher than the lowest triplet state ($^3L_a$). In some cases, calculations predict that additional triplet states lie in between the $^3L_b$ and $^3L_a$ states. Intersystem crossing from $^1L_b$ to the degenerate triplet might be the important path for all the hydrocarbons in Table XI, since in all cases the lowest singlet is $^1L_b$. At any rate, since it is very likely that more than one triplet state lies below the lowest singlet , the total rate of intersystem crossing is a sum over more than one path. Therefore, contrary to Kasha's suggestion, there is no reason to expect a simple correlation of intersystem crossing rates with the $S_1$-$T_1$ energy gap. From the meager data in Table XI, it is difficult to decide whether, in fact, there is any simple relationship between the relative rates and the energy gap. Furthermore, the oscillator strengths listed could easily be in error by a factor of 2.

A brief note about naphthalene closes this section. The intersystem crossing yield for naphthalene-$d_8$ is the same as that for naphthalene. Thus, deuterium substitution in naphthalene does not affect the rates of any of the processes originating in the $S_1$ state. This finding is supported by some results of de Groot and van der Waals (28). They found that the fluorescence yields of naphthalene and naphthalene-$d_8$ are the same to within 10%.

Benzene

The very accurate determination of the low temperature (EPA, 77°K) emission yields for benzene, $\varphi_p = \varphi_f = 0.20 \pm 0.02$, carried out by Lim (14) puts the intersystem crossing yield for benzene, under these conditions, on a firm basis. The phosphorescence lifetime of benzene in EPA at 77°K is 7 sec, and that of benzene-$d_6$ $28 \pm 2$ sec. If the latter is taken as the true radiative lifetime, then $\varphi_{ic} = \frac{28}{7}(0.20) = 0.80$ and $1 - (\varphi_{ic} + \varphi_f) \simeq 0$. Ishikawa and Noyes (81) carried out measurements of the benzene sensitized phosphorescence of biacetyl in the gas phase at room temperature. Their results give indirect but compelling evidence for triplet benzene being formed in high yield in the gas phase. However, attempts to study benzene triplets in fluid solution have yielded confusing results.

Although hard sought, triplet-triplet absorption has not been observed for benzene either in fluid solution (83) or in glassy solution at 77°K (22), excluding flash photolysis as a tool for studying benzene triplets. Recently Dubois and Wilkinson (84) reported their attempts to study benzene triplets in fluid solution by sensitizing biacetyl fluorescence and phosphorescence in hexane solution at room temperature using benzene as donor. Electronic energy transfer from the lowest excited singlet state of benzene to biacetyl producing either the first or second excited singlet state of biacetyl proceeds with a diffusion controlled rate. No evidence for energy transfer from benzene to biacetyl was found in fluid solution. However, in EPA at 77°K, transfer of excitation from triplet benzene to biacetyl was easily established. Shortly afterward, Lipsky (85) reported his results from an almost identical study. In this case, energy transfer from triplet benzene to biacetyl was observed in fluid solution (cyclohexane at 25°C). Furthermore, Lipsky found that a transient built up in the solution during irradiation which efficiently quenched the benzene triplets. This explains the negative results of Dubois and Wilkinson. Evidence for the transient quencher derives from the following observations. The intensity of the sensitized biacetyl phosphorescence decayed rapidly with time of irradiation approaching (in about one minute) a constant value of about half the initial intensity. This time dependence is absent in the fluorescent emission from benzene and also is not observed if biacetyl is directly excited to either its first or second excited singlet level. Thus, the transient quenches benzene triplets but not benzene singlets or biacetyl singlets or triplets. Recovery of initial biacetyl phosphorescent intensity is obtained if the irradiation is interrupted for a short time. Lipsky suggests that the transient quencher is a photodecomposition product of biacetyl, but he did not suggest a structure for it. Although biacetyl does decompose in the gas phase when irradiated with light of wavelengths ≤3130 Å (86), this decomposition is far less efficient in solution. Furthermore, the gas phase decomposition products do not quench benzene triplets (82). It is also difficult to imagine a photoproduct of biacetyl which would have the characteristics required of the transient quencher. The possibility that the quencher is a photoproduct of benzene has not been examined, even though several reports concerning photochemical reactions of benzene and benzene derivatives in the condensed phase have appeared in the literature (87, 88, 89, 90).

The intersystem crossing yield measured for benzene using *cis*-piperylene as a quencher is 0.24 ± .01. An important difference between the piperylene experiments and the experiments using biacetyl as quencher is that the latter was present in concentrations of $10^{-5} - 10^{-3}$ M, whereas 0.01 - 0.05 M piperylene was employed. Thus, whereas a transient quencher arising from excited benzene would successfully compete with the biacetyl for benzene triplets, it might not be able to compete with piperylene quenching of benzene triplets. It is possible, therefore, that at room temperature 24 per cent of benzene singlets undergo intersystem crossing, ~11 per cent undergo fluorescent emission (10), and the remainder undergo a "chemical" isomerization leading to a short-lived high-energy isomer which is capable of efficiently quenching benzene triplets. The isomerization requires an activation energy and does not occur at 77°K.

As previously discussed, there is precedent for an activated "chemical" isomerization as a path for decay from an excited singlet state (69). *Cis*-stilbene fluoresces in glassy solution at 77°K, but in fluid solution at room temperature no fluorescence is observed. Instead an isomer, dehydrophenanthrene (91), is formed which is not formed at 77°K. *"Chemical" isomerization paths leading to short-lived high-energy isomers which thermally revert to the original ground state molecule may play an important role in the deactivation of the excited states of many organic systems*.

## Aromatic Amines

Ermolaev has pointed out (13) that the rate of intersystem crossing in the amino derivatives of benzene must be two orders of magnitude greater than in the hydrocarbons benzene or toluene. Data concerning intersystem crossing in five aromatic amines is listed in Table XII. From oscillator strengths and low temperature emission data, one can estimate relative intersystem crossing rates for aniline and benzene of 0.3 and 0.008, respectively.

# TABLE XII

## Intersystem Crossing in Aromatic Amines

| Compound | $E_{T_1}(cm^{-1})$ [a] | $\Delta E_{S_1-T_1}(cm^{-1})$ [b] | $\varphi_{ic}$ | $f_{S_1-S_0}$ [c] | Rel. $k_{ic}$ [d] | $\varphi_p/\varphi_f$ [e] | $\tau_p$(sec) [e] |
|---|---|---|---|---|---|---|---|
| Aniline | 26,800 | 6,200 | --- | 0.05 | ~0.15[f] | 3.1 | 4.2 |
| Diphenylamine | 25,050 | 6,000 | 0.38 | 0.4 | 0.25 | 7.3 | 1.9 |
| Triphenylamine | 24,500 | 5,500 | 0.88 | 0.5 | 3.7 | 15 | 0.7 |
| Carbazole | 24,500 | 3,700 | 0.36 | 0.05 | 0.028 | 0.6 | 7.6 |
| 1-Naphthylamine | 20,100 | 9,800 | 0.15 | [0.05][g] | [0.009] | --- | 1.5 |

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a. O'-O band energy from phosphorescence spectra at low temperatures (49).

b. These are approximate energy differences between the O'-O bands of fluorescence and phosphorescence.

c. Estimates from room temperature absorption spectra using $f = 4.3 \cdot 10^{-9} \int \epsilon d\nu$.

d. Calculated from rel. $k_{ic} = f(\frac{\varphi_{ic}}{1-\varphi_{ic}})$.

e. Data of Ermolaev for samples in an ether alcohol glass at 77°K (13).

f. Calculated from rel. $k_{ic} = f(\varphi_p/\varphi_f)$.

g. The two lowest singlet states are not resolved in the absorption spectrum (95). This value is half of the estimated combined oscillator strengths for the transitions to both lowest singlet states.

Diphenylamine exhibits an intersystem crossing rate nearly equal to that of aniline. One can estimate a maximum relative $k_{ic}$ for triphenylmethane [$f_{S_1-S_0}$ = 0.015 (77); $\varphi_f$ = 0.23 (10)]of 0.045, or about two orders of magnitude smaller than that of triphenylamine. On the other hand, the intersystem crossing rate calculated for carbazole is not different from that calculated for fluorene and is only three times larger than that for phenanthrene. The estimated rate for 1-naphthylamine is about three times larger than that calculated for 1-methylnaphthalene (rel. $k_{ic}$ = 0.003). The enhanced intersystem crossing rates in the anilines compared with the hydrocarbons cannot be due just to the presence of an amino nitrogen, since this large enhancement does not seem to be present in carbazole or 1-naphthylamine.

Assignments of the lower excited singlet levels in aniline and its derivatives are still open for question. Some investigators feel that the intense long-wavelength (2800-3000 Å) absorption band of the anilines is a displacement of the long-wavelength band of benzene (92). However, Klevens and Platt (93) associate the second absorption band of aniline with the long-wavelength band of benzene. Murrell (94) and Ermolaev (13) go on to assign the long-wavelength band in the anilines as an "intramolecular charge-transfer" band. Furthermore, Ermolaev (13) associates this charge-transfer band with the large phosphorescence yields exhibited by these compounds.

Similar intense long-wavelength bands do not seem to appear in the naphthylamines (95) or in carbazole. The absorption spectrum of the latter seems more analogous to that of phenanthrene rather than to that of fluorene. Thus, the fast intersystem crossing in the anilines does seem to be associated with the presence of an intense long-wavelength absorption band assigned by some investigators to a transition involving significant charge-transfer from the amino nitrogen to the ring. Very fast intersystem crossing may occur because of a large spin-orbit coupling in this so-called "charge-transfer" state or because of the close proximity of an associated triplet state,* or for both reasons. It should be mentioned that intersystem crossing is greatly enhanced by the formation of intermolecular charge-transfer complexes (96).

The diphenylamines undergo an interesting rearrangement to a dihydrocarbazole upon excitation in solution at room temperature (97). This rearrangement occurs only from the triplet state of the diphenylamine, but at a rate such that with 0.05 M quencher, triplet quenching should prevent the rearrangement process (97). In the presence of oxygen the dihydrocarbazole is converted to the

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* Since saturated substituents have a relatively small effect on the triplet states even when significant charge transfer is present in the singlet state, the phosphorescent states for all the compounds in Table XII is probably a $\pi,\pi^*$ state very similar to that found in the corresponding hydrocarbon.

carbazole. However, at lower temperatures (~ -70°C), the dihydrocarbazole decomposes to give the carbazole and a hydrogen molecule by a temperature-independent process with high quantum efficiency (~0.2). At room temperature, in the absence of oxidizing agents, the dihydrocarbazoles revert to the diphenylamines. These systems, then, clearly demonstrate "chemical" paths for triplet decay.

## Quinoline

In quinoline, the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ lowest singlet states are located close together, with the $n \rightarrow \pi^*$ state lowest in the vapor state (98) as well as in hydrocarbon solvents (99). In hydroxylic glasses, due to hydrogen bonding of the nitrogen non-bonded electron pair, the two states interchange position. On going from hydrocarbon glasses to hydroxylic glasses, because of the interchange of the lowest singlet states, the emission characteristics of quinoline change from being a phosphorescent-nonfluorescent molecule to a phosphorescent-fluorescent molecule (99, 100). The phosphorescent emission and lifetime is the same in both glasses, and closely resembles that of naphthalene. Thus, the lowest triplet state is a $\pi \rightarrow \pi^*$ state. Finally, El-Sayed (31) presents arguments for placing the lowest $n \rightarrow \pi^*$ triplet state in between the $\pi \rightarrow \pi^*$ triplet state and the singlet states. El-Sayed's argument is based on his calculations which showed that in nitrogen heterocyclics the spin-orbit coupling and rates of intersystem crossing from an n→π* state to a π→π* state, or vice versa, are much larger than those from an n→π* state to an n→π* state, or those from a π→π* state to a π→π* state. In hydrocarbon solvents where the n→π* singlet is lowest, intersystem crossing from this state overwhelms fluorescence not because intersystem crossing is very fast, but because fluorescence from the n→π* singlet is very slow. From comparisons of the absorption and emission characteristics of quinoline and naphthalene in EPA, El-Sayed concludes that the rate of intersystem crossing must be enhanced (~1000 times) in quinoline as compared to naphthalene. He attributes this "to the triplet n→π* state which is located between the lowest singlet and triplet π→π* states in quinoline."

The first attempts to measure the intersystem crossing yield of quinoline in benzene gave 0.16 as the result. In view of the reports that no fluorescence is observed from quinoline in hydrocarbon solvents, this value seemed low. Upon testing, the benzene solvent was found to contain water, probably of sufficient quantity to complex all the quinoline in the solution. This is not surprising, since benzene can easily dissolve up to 1 M water. Using benzene which was dried with lithium aluminum hydride, redetermination of the intersystem crossing yield gave the value 0.31. Whether the solutions were completely free of water is not known. Unfortunately, absorption spectra of the various quinoline solutions were not recorded. If 0.31 is an accurate value for the intersystem crossing yield of quinoline in dry hydrocarbon solvent, then at room temperature other radiationless decay processes from the singlet state must occur 70 per cent of the time, since no fluorescence is observed from quinoline in dry hydrocarbon solvents even at 77°K. Until further experiments are performed, this high efficiency of radiationless $S_1$ decay is attributed to small amounts of water and perhaps phenol present in the solvent. There is some evidence that "chemical" decay paths probably operate when hydroxylic substances are present. El-Sayed (31) pointed out that the fluorescence yield for quinoline in EPA at 77°K is an order of magnitude smaller than that for naphthalene, although the radiative lifetime of quinoline fluorescence is much smaller than that for naphthalene and the phosphorescence yields are comparable. He attributes the decrease of the fluorescence yield in quinoline to a radiationless process which could be predissociation, auto-ionization, photoreaction, or radiationless $S_1 \rightarrow S_0$ decay. Ermolaev and Kotlyar (100) found that fluorescence from quinolinium ion $C_9H_8N^+$ is readily detected upon irradiation of quinoline in glasses containing small amounts of methanol, ethanol, or water. Furthermore, the intensity of quinoline fluorescence and phosphorescence decreases with exposure in these solutions. The addition of small amounts of phenol quenches all quinoline emission.

The determination of emission characteristics and intersystem crossing and emission yields for quinoline in various carefully controlled solvent environments would elucidate the nature and extent of the "chemical" decay paths in quinoline. Solvent effects on the intersystem crossing yields of the aromatic amines discussed in the previous section should also be checked, since it is known that photoionization takes place upon excitation of some of these compounds in hydroxylic glasses at low temperatures (101).

## Aromatic Carbonyl Compounds

It was recognized very early that intersystem crossing in aromatic carbonyl compounds must be fast compared with that in most aromatic hydrocarbons (4). This conclusion was based on the fact that although radiative lifetimes of the lowest singlet states in the carbonyl compounds are comparable to the radiative lifetimes of related hydrocarbon singlet states, high phosphorescence yields and very little or no fluorescence was observed for the carbonyl compounds. Table XIII contains the intersystem crossing yields measured for some aromatic carbonyl compounds along with calculated lower limits for relative intersystem crossing rates. The latter are all about ten or more times greater than those calculated for most of the hydrocarbons in Table XI. All that can be said about

## TABLE XIII

### Intersystem Crossing in Aromatic Carbonyl Compounds

| Compound | $E_{T_1}$ (cm$^{-1}$)[a] | $\Delta E_{S_1-T_1}$ (cm$^{-1}$)[b] | $\varphi_{ic}$ | $f_{S_1 \rightarrow S_0}$[c] | Rel. $k_{ic}$[d] | $\tau_p$(sec)[g] |
|---|---|---|---|---|---|---|
| Benzophenone | 23950 | 2700 | 1.00 | 0.003 | ≥3 | 0.005 |
| Acetophenone | 25700 | 2300 | 1.00 | 0.001 | ≥1 | 0.008 |
| Fluorenone | 18650 | 4000 | 0.93 | 0.01 | 0.13 | --- |
| Benzil | 18800 | 4200 | 0.92 | 0.003 | 0.04 | 0.005 |
| Anthraquinone | 21800 | 1800 | 0.90 | 0.005[e] | 0.05 | 0.004 |
| 2-Acetonaphthone | 20700 | 6300 | 0.84 | ---[f] | --- | ~1.0[h] |
| Michler's ketone[k] | 21300 | 3000 | 1.00 | ---[j] | --- | ~0.3[i] |

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a. O'-O band energies from phosphorescence spectra (49).

b. Approximate energy difference between the O'-O band of the phosphorescence spectrum and the long-wavelength bandhead of room temperature absorption spectrum.

c. Estimated from room temperature absorption spectra in non-polar solvents using $f = 4.3 \times 10^{-9} \int \epsilon d\nu$

d. Calculated from $k_{ic} = f(\varphi_{ic}/1-\varphi_{ic})$.

e. This is a very rough estimate due to severe overlapping of the lowest singlet states.

f. The two lowest singlet states lie so close that an estimate of $f_{S_1 \rightarrow S_0}$ from the absorption spectrum is not possible.

g. Data of Parker and Hatchard for samples in EPA at 77°K (18).

h. Data of Ermolaev (102).

i. Data of Pitts et al. (103).

j. See text for a discussion of the absorption spectrum of this compound.

k. p, p'-bis(dimethylamino)benzophenone.

benzophenone and acetophenone from the measured intersystem crossing yields is that they undergo intersystem crossing at least one-hundred times faster than they fluoresce. However, since essentially no fluorescence has been detected from these compounds (11, 15, 18)*, it is probably safe to say that they undergo intersystem crossing at least one-thousand times faster than they fluoresce.

The lowest excited singlet states of benzophenone, acetophenone, and benzil are $n \rightarrow \pi^*$ states, the excitation being "localized" in the region of the carbonyl groups (104, 105). In anthraquinone and fluorenone, the lowest excited singlet is probably an $n \rightarrow \pi^*$ state (104, 105), with a more delocalized nature. In 2-acetonaphthone, the lowest $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states lie very close together, with the $n \rightarrow \pi^*$ state probably the lowest lying excited singlet state. The close proximity of the two states precludes determination of oscillator strengths from the room temperature absorption spectrum of 2-acetonaphthone. The first absorption band of Michler's ketone (p-p'-bis(dimethylamino)benzophenone) is centered about 3500 Å and has an $\epsilon_{max}$ of about 25,000. This strong absorption is probably due to the "charge-transfer" type transition observed in other aniline derivatives, vide supra. The carbonyl $n \rightarrow \pi^*$ transition

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* It is assumed that if $\varphi_f = 0.01$, fluorescence would have been detected.

is completely buried under this strong band. Which transition has the lower transition energy is not known for certain.* If the carbonyl n→π* state is the lowest excited singlet state in benzene solution, then Michler's ketone is best treated as a derivative of benzophenone. Unfortunately, a comparison with benzophenone is impossible, not only because the oscillator strength for the n→π* transition in Michler's ketone cannot be experimentally determined, but also because only lower limits to the relative intersystem crossing rates can be calculated for both Michler's ketone and benzophenone. That is, the available data for benzophenone do not allow one to decide between relative intersystem crossing rates of 3 or 3000** for benzophenone.

Assignments of the lowest triplet states of some of the aromatic carbonyl compounds in Table XIII have been made. Although the legitimacy of the various criteria (lifetimes, solvent effects, vibronic structure of emission spectrum, etc.) used to differentiate

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[*] A weak, short-lived emission beginning near 4000 Å and extending past the onset of the phosphorescence observed (8) from samples of Michler's ketone in EPA might be a fluorescence from the compound. This emission is not observed (8) from samples dissolved in a hydrocarbon glass. Thus, in hydrocarbon solvents the lowest excited singlet state might be the carbonyl n→π* state, whereas in hydroxylic solvents the aniline-type state might be lowest.

[**] A rel. $k_{ic}$ of 3000 corresponds to a rate constant near $10^{12}$ $\mathrm{sec}^{-1}$ which approaches the rate ($10^{12}$-$10^{13}$ $\mathrm{sec}^{-1}$) of vibrational relaxation in the condensed phase.

between $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplets is open to question, assignments of the lowest triplet states of the remaining compounds in Table XIII can be made. The phosphorescent state of both benzophenone and acetophenone is undoubtedly an $n \rightarrow \pi^*$ triplet (103, 104, 105, 106). The phosphorescence spectrum of 2-acetonaphthone resembles that of naphthalene (8) and the triplet lifetimes are similar. Thus, the lowest triplet state in 2-acetonaphthone is $\pi \rightarrow \pi^*$. This fact is reflected in its lack of ability to abstract a hydrogen atom from isopropyl alcohol (107). On the basis of the phosphorescent lifetime (18), the solvent effects on the phosphorescence spectrum (49), and the hydrogen abstracting ability (108), the lowest triplet state of anthraquinone is probably an $n \rightarrow \pi^*$ state. The lowest triplet of benzil exhibits similar characteristics (8), and is also assigned as an $n \rightarrow \pi^*$ triplet. Only very weak phosphorescence can be detected from fluorenone (8). A lower limit to the radiative lifetime of the fluorenone triplet can be estimated from the triplet lifetime measured by the flash photolytic technique. This lifetime is $3 \times 10^{-4}$ sec (109), and so the radiative lifetime is at least 0.3 sec. Furthermore, fluorenone is not photoreduced in isopropanol (110). On this basis, a lowest $\pi \rightarrow \pi^*$ triplet is assigned. Michler's ketone is not photoreduced in isopropyl alcohol and exhibits a long phosphorescent lifetime compared with that of benzophenone. The lowest triplet of Michler's ketone is probably a $\pi \rightarrow \pi^*$ state.

Table XIV shows the tentative assignments for the lowest singlet and triplet states of the carbonyl compounds along with the relative intersystem crossing rates. It is evident that no correlation exists between the nature of the lowest triplet state and the intersystem crossing rate, even though all the compounds listed have the same kind ($n \rightarrow \pi^*$) of lowest excited singlet state (with the possible exception of Michler's ketone). In the cases of fluorenone, 2-acetonaphthone, and Michler's ketone, there must also be an $n \rightarrow \pi^*$ triplet below the lowest singlet. Whether there are other triplets below the lowest singlets of benzophenone, acetophenone, benzil, and anthraquinone is not known. The treatment of spin-orbit coupling matrix elements in nitrogen heterocyclics given by El-Sayed (31) should also approximately apply to the aromatic carbonyl compounds, and so the low rate of intersystem crossing in fluorenone and 2-acetonaphthone may be due to the fact that it occurs between $n \rightarrow \pi^*$ states. In benzophenone and acetophenone, a $\pi \rightarrow \pi^*$ triplet might lie below the $n \rightarrow \pi^*$ singlet, and fast intersystem crossing results. In benzil and anthraquinone, the crossing might be occurring from the lowest $n \rightarrow \pi^*$ singlet to the lowest or higher $n \rightarrow \pi^*$ triplet (there should be two low-lying $n \rightarrow \pi^*$ triplets) and a slow rate results. An investigation into the natures and positions of other low-lying aromatic carbonyl triplet states would be very profitable.

## TABLE XIV

### Assignments of Lowest Excited States for Aromatic Carbonyl Compounds in Hydrocarbon Solvents

| Compound | $S_1$ | $T_1$ | Rel. $k_{ic}$[a] |
|---|---|---|---|
| Benzophenone | $n \rightarrow \pi^*$ | $n \rightarrow \pi^*$ | $\geq 3$ |
| Acetophenone | $n \rightarrow \pi^*$ | $n \rightarrow \pi^*$ | $\geq 1$ |
| Benzil | $n \rightarrow \pi^*$ | $n \rightarrow \pi^*$ | 0.005 |
| Anthraquinone | $n \rightarrow \pi^*$ | $n \rightarrow \pi^*$ | 0.13 |
| Fluorenone | $n \rightarrow \pi^*$ | $\pi \rightarrow \pi^*$ | 0.004 |
| 2-Acetonaphthone | $n \rightarrow \pi^*$ | $\pi \rightarrow \pi^*$ | [0.03][b] |
| Michler's ketone | ? | $\pi \rightarrow \pi^*$ | ? |

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a. From Table XIII.

b. Assuming $f_{S_1 \rightarrow S_0} \approx 0.005$.

Finally, it must be kept in mind that vibrational factors have not been considered in this discussion. Furthermore, in none of the discussions about relative intersystem crossing rates have vibronic coupling effects been mentioned. Apart from direct spin-orbit interactions, there are three additional mechanisms for the spin-forbidden transition: direct spin-vibronic coupling (a very weak, though first-order term); spin-orbit coupling with vibronic coupling in the singlet manifold; and vibronic coupling in the triplet manifold with spin-orbit coupling (32, 111). Vibronic coupling may be an important consideration in explaining, for example, the enhanced rate of intersystem crossing in benzophenone and acetophenone over that in fluorenone and anthraquinone. The latter pair are more vibrationally constrained than the former pair.

A discussion of radiationless deactivation paths for the singlet states of the carbonyl compounds other than intersystem crossing closes this section. Other radiationless deactivation paths are precluded for benzophenone, acetophenone, and Michler's ketone (in hydrocarbon solvent), since intersystem crossing is totally efficient in those cases. This also means that the long-lived transient observed (112) when a benzene solution of benzophenone is irradiated ($\varphi$ = .1) arises from the benzophenone triplet. Fluorescence was easily observed from samples of fluorenone, anthraquinone, and benzil in benzene (containing a triplet quencher). Thus, little radiationless $S_1 \rightarrow S_0$ deactivation or photoreaction involving the singlet state occur in these cases. However, 2-acetonaphthone does not exhibit appreciable fluorescence, and so other radiationless deactivation paths beside intersystem crossing may operate here.

## Naphthalene Derivatives

Table XI contains the available data concerning intersystem crossing in some naphthalene derivatives. Substitution at the 1-position of naphthalene causes, in general, a small increase in intensity of the long-wavelength band due to the reduction of symmetry in the molecule. This is accompanied by a relatively small bathochromic shift. However, the second absorption band usually undergoes a much larger bathochromic shift resulting in severe overlap of the two bands. It is therefore impossible to obtain oscillator strengths for the $S_1 \rightarrow S_0$ radiative transition from the absorption spectra of many of the 1-substituted naphthalenes. In some cases, however, rough estimates can be obtained.

With the exception of 2-acetonaphthone, which was discussed in the previous section, the highest intersystem crossing yield measured for a naphthalene derivative was 0.63 (1-fluoronaphthalene) and the lowest 0.15 (1-naphthylamine). The $S_1 \rightarrow S_0$ oscillator strengths for all the compounds in Table XV probably do not vary over more than a factor of four. All the relative intersystem

# TABLE XV

## Intersystem Crossing in Naphthalene Derivatives

| Compound | $E_{T_1}$ (cm$^{-1}$)[a] | $\Delta E_{S_1 \rightarrow T_1}$ (cm$^{-1}$)[b] | $\varphi_{ic}$ | $f_{S_1 \rightarrow S_0}$[c] | Rel. $k_{ic}$[e] | $\tau_p$(sec)[f] |
|---|---|---|---|---|---|---|
| Naphthalene | 21,250 | 10,500 | 0.39 | 0.002 | 0.001 | 2.3 |
| 1-Methylnaphthalene | 21,000 | 10,500 | 0.48 | 0.003 | 0.003 | 2.1 |
| 2-Methylnaphthalene | 20,800 | 10,500 | 0.51 | | | |
| Acenaphthene | 20,800 | 10,200 | 0.47 | ~0.01[d] | ~0.01 | |
| 1-Fluoronaphthalene | 21,150 | 10,300 | 0.63 | | | 1.5 |
| 1-Naphthol | 20,600 | 10,800 | 0.27 | ~0.01[d] | ~0.003 | 1.9 |
| 1-Methoxynaphthalene | 20,900 | 10,000 | 0.26 | ~0.01[d] | ~0.0003 | |
| 1-Naphthylacetate | 20,750 | 10,100 | 0.29 | | | |
| 1-Naphthoic Acid | 20,200 | 10,200 | 0.20 | | | |
| 1-Naphthonitrile | 20,100 | 10,000 | 0,17 | | | |
| 1-Naphthylamine | 20,100 | 9,800 | 0.15 | ~0.05 | ~0.01 | 1.5 |

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a. O'-O band positions from phosphorescence spectra (EPA tt°K) (8).

b. Approximate energy gaps between the O'-O bands from the fluorescence and phosphorescence spectra.

c. Estimated from room temperature absorption spectra using $f = 4.3 \times 10^{-9} \int \epsilon \, d\nu$.

d. Rough estimates.

e. Calculated from $k_{ic} = f \left( \frac{\varphi_{ic}}{1-\varphi_{ic}} \right)$.

f. From data of Ermolaev and Svitashev (12).

crossing rates probably lie in the range 0.001-0.01.

In order to obtain quantitative information about the heavy atom effect (76) upon intersystem crossing in naphthalene, attempts were made to obtain the intersystem crossing yields for 1-chloro-, 1-bromo-, and 2-bromonaphthalene. Unfortunately, all three compounds are not photostable (108). The photodecomposition products catalyzed the thermal isomerization of the olefins used, and so no intersystem crossing yields could be determined.

## Concluding Remarks

The experimental method for "counting" triplets described in this thesis is an example of "chemical spectroscopy," a term coined in these laboratories. "Chemical spectroscopy" is defined as the use of bimolecular sensitization and quenching, and photochemical reactions as tools in determining the electronic structure and geometry of molecules in electronically excited states, in elucidating deactivation paths for excited molecules, and in resolving the details of energy transfer processes. The coupling of optical and "chemical" spectroscopy leads to detailed information concerning both spectroscopic and non-spectroscopic molecular electronic states and interconversions between them. However, large-scale exploitation of this powerful combination has not yet arrived. It is the hope of this writer that the work described herein represents another demonstration of the sensitivity, simplicity, and usefulness of "chemical spectroscopy," and that it will enhance the use of "chemical" methods among spectroscopists.

# EXPERIMENTAL

## Materials:

### Olefins:

*cis*-Piperylene was Matheson, Coleman and Bell technical grade and contained *trans*-piperylene and cyclopentene as major impurities. The *trans*-isomer was eliminated by the method of Craig (113) and separation of *cis*-piperylene from cyclopentene was effected by preparative vapor phase chromatography on 12 ft x 3/8 in diameter columns containing 1,2,3-*tris*-[2-cyanoethoxy]propane on Chromosorb using a Beckman Megachrom. The *cis*-piperylene was distilled before use. Depending on the number of chromatographic passes, the *cis*-piperylene contained from 0.05 to 0.15% of the *trans*-isomer and from .05 to 1% of cyclopentene as impurities.

*trans*-Piperylene was Matheson, Coleman and Bell technical grade and contained *cis*-piperylene and cyclopentene as major impurities. Separation of the *trans*-isomer was effected by preparative vapor phase chromatography on 12 ft x 3/8 in diameter columns containing 1,2,3-*tris* [2-cyanoethoxy]propane on Chromosorb using a Beckman Megachrom. Four chromatographic passes afforded *trans*-piperylene containing no detectable amount of cyclopentene and 0.03% of *cis*-piperylene. The *trans*-piperylene was distilled before use.

trans-β-Methylstyrene was synthesized by Dr. R. Steinmetz and purified by preparative vapor phase chromatography and vacuum distillation. The material contained only 0.12% of the cis-isomer as an impurity.

trans-α-Methylstilbene. Samples of purified trans-α-methylstilbene were generously supplied by Professor D. J. Cram and Mr. D. H. Hunter. The samples contained 0.35% of the cis-isomer as the only detectable impurity.

Sensitizers:

Benzophenone (Matheson, Coleman and Bell, Reagent Grade) was recrystallized twice from diethyl ether. It melted at 48-48.5° (uncorrected).

Acetophenone (Matheson, Coleman and Bell, Reagent Grade) was distilled under reduced pressure. The fraction boiling at 35-36° (1 mm) was collected for use.

9, 10-Anthraquinone (Eastman, Sublimed) was twice recrystallized from benzene.

Fluorenone (Matheson, Coleman and Bell, Reagent Grade) was obtained from Dr. J. Saltiel. It had been recrystallized twice from n-heptane and melted at 84.3-84.7° (hot stage).

Benzil (Matheson, Coleman and Bell, Reagent Grade) was recrystallized twice from n-hexane. It melted at 96-97° (uncorrected hot stage).

2-Acetonaphthone (Eastman, White Label) was recrystallized from ligroin (60-70° b.p. range). It melted at 53-54° (uncorrected hot stage).

Naphthalene (Matheson, Coleman and Bell, Reagent Grade) was recrystallized from n-hexane and then twice sublimed. For most of the determinations the naphthalene used was purified by zone refining performed by Mr. W. Herkstroeter.

Benzene was Phillips Research Grade, 99.93 mole % pure, and was used without further purification.

1-Methylnaphthalene (Calbiochem, Reagent) was passed through an alumina column prior to use.

2-Methylnaphthalene (Calbiochem, Reagent) was sublimed under reduced pressure. It melted at 37-38° (uncorrected hot stage).

Acenaphthene (Matheson, Coleman and Bell, Reagent Grade) was twice sublimed under reduced pressure. It melted at 94.5-95.0° (uncorrected hot stage).

Fluorene (Matheson, Coleman and Bell, Reagent Grade) was twice sublimed under reduced pressure. It melted at 114-115° (uncorrected hot stage).

Phenanthrene (Matheson, Coleman and Bell, Reagent Grade) was treated with maleic anhydride to remove the anthracene and then recrystallized twice from ethanol. The purification was performed by Mr. W. Hardham.

Triphenylene (Aldrich, Reagent) was not further purified.

p-Bromobenzophenone was obtained from Dr. D. O. Cowan. It had been purified by alumina chromatography followed by recrystallization from n-hexane.

p-Methylbenzophenone (Eastman, White Label) was twice recrystallized from pentane. It melted at 59-60° (uncorrected hot stage).

Chrysene (Matheson, Coleman and Bell, Reagent Grade) was sublimed under reduced pressure.

1,2,5,6-Dibenzanthracene (Eastman) was sublimed under reduced pressure.

Thioxanthone (Aldrich, Research Grade) was purified by alumina chromatography with benzene as eluent, treatment with carbon black in methyl alcohol, and recrystallization from methanol. It melted at 209.0° (uncorrected hot stage).

Carbazole (Eastman, Reagent Grade) was recrystallized from benzene and then sublimed under reduced pressure. It melted at 239-240° (uncorrected hot stage).

Diphenylamine (Eastman, Reagent Grade) was sublimed under reduced pressure. It melted at 53.5-54° (uncorrected hot stage).

Triphenylamine (Eastman, Reagent Grade) was recrystallized from ethanol and then sublimed under reduced pressure. It melted at 125-126° (uncorrected hot stage).

*Michler's ketone* (4,4′-*bis*-dimethyaminobenzophenone) (Eastman, Practical Grade) was recrystallized twice from methanol. It melted at 171-172° (uncorrected hot stage).

*1-Fluoronaphthalene* (Eastman, Reagent Grade) was passed through an alumina column just before use.

*1-Naphthol* (Eastman, Reagent Grade) was recrystallized from ethyl alcohol. It melted at 92-93° (uncorrected hot stage).

*1-Naphthyl acetate* was prepared by refluxing 1-naphthol (technical grade) in a large excess of acetic anhydride for three hours. After pouring the reaction mixture over ice, the product was extracted with ether. The ether solution was washed with 10% aqueous sodium carbonate, then with water, and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and the residue recrystallized twice from ethanol to yield 1-naphthyl acetate as white needles melting at 44.5-45° (uncorrected hot stage).

*1-Naphthylamine* (Eastman, Technical Grade) was twice sublimed under reduced pressure, recrystallized from ethyl alcohol, and sublimed again. It melted at 49-50° (uncorrected hot stage).

*1-Naphthonitrile* (Eastman, Technical Grade) was recrystallized twice from pentane. It melted at 37-38° (uncorrected hot stage).

1-Naphthoic acid (Eastman, Reagent Grade) was twice recrystallized from methyl alcohol. It melted at 159-160° (uncorrected hot stage).

1-Methoxynaphthalene (Eastman, Reagent Grade) was twice recrystallized from ethyl alcohol.

Quinoline (Eastman, Practical Grade) was twice distilled through an efficient column under reduced pressure, once from zinc dust and once from a mixture of barium oxide and zinc dust. Each time a middle fraction was collected for use.

## Solvents:

Benzene. Phillips Research Grade, 99.93% mole purity, benzene was used throughout the study. Although the manufacturers' label claimed the major impurity to be toluene, no trace of toluene could be found by analytical vapor phase chromatography employing a flame ionization detector. Trace amounts of saturated hydrocarbons were noticed. The benzene did contain a small amount of water. The benzene was dried for the quinoline experiments in the following manner. A glass apparatus containing two bulbs was constructed. Benzene (30 ml) and lithium aluminum hydride (about 1 gram) were placed in one bulb. The system was then degassed by the freeze-pump-thaw method (4 cycles). The thaw periods were 1/2 hr long to allow as complete reaction as possible between the water present and the $LiAlH_4$. The system was finally sealed under vacuum. The benzene was distilled from bulb containing the $LiAlH_4$ into the empty bulb and then poured back to the bulb containing the $LiAlH_4$. This was repeated seven times. After the final distillation into the empty bulb, the benzene was frozen and the bulb sealed and removed from the rest of the system. The dried benzene was stored in the sealed bulb until use.

*trans*-1,2-Dimethylcyclohexane. Phillips Pure Grade *trans*-1,2-dimethylcyclohexane was washed with an equal volume of concentrated sulfuric acid by stirring the mixture for three hours. This procedure was repeated three times. After washing with aqueous sodium bicarbonate and then with water, the solvent was dried over anhydrous magnesium sulfate. The dried solvent was carefully distilled through a spinning band column and stored in the refigerator. The *trans*-1,2-dimethylcyclohexane was distilled again (spinning band column) just prior to use. A one centimeter path of the purified solvent exhibited an optical density of $< 0.05$ at 2537 Å.

## Sample Preparation:

Appropriate amounts of the sensitizers were placed in 10 ml volumetric flasks. A fresh stock benzene (or 1,2-*trans*-dimethylcyclohexane) solution of the olefin was then added to the mark. This method insured that all the samples in a run contained the same amount of olefin. Enough sensitizer was used to achieve a sample optical density of 3-4 at the excitation wavelength.

Identical aliquots (3.6 ml) of the solutions were loaded into the sample tubes by means of a spring-loaded syringe. Two samples of each solution were prepared. The sample tubes consisted of either 13 x 100 mm or 15 x 125 mm pyrex culture tubes sealed to 12/30 standard taper female joints and constricted at a point about three inches from the bottom. In some runs, the tubes were modified by inclusion of a small trap which prevented contamination of the reaction mixtures by stopcock grease from the vacuum system. In all cases the tubes were carefully washed and dried. The samples were degassed with three or four freeze-degas (to about $5 \times 10^{-4}$ mm pressure)-thaw cycles. After degassing, the tubes were sealed at the constriction. The sample tubes were stored in the dark when not in use. An extra benzophenone sample for use in an unirradiated blank was prepared for each run.

## Irradiation of Samples

Two different irradiation apparatuses were employed. The apparatus most extensively used has been previously described in detail (106). Generally, the light from a Westinghouse (SAH-800c) 800-watt medium pressure mercury lamp is collimated by using mirrors, and the beam passed down an optical bench. The sample tubes (4) held in a Beckman u.v.-cell holder can be placed in the beam. Glass filters and/or quartz cells containing filter solutions can be placed between the lamp and the samples. Since the beam intensity was not constant across the face of the cell holder, it was necessary to interchange the samples periodically (usually eight times during a run) so that each sample spent the same amount of time in each position in the cell holder. This apparatus will be called the "optical bench" throughout the remainder of this section.

Some of the irradiations were carried out in the "merry-go-round" apparatus designed by Mr. F. G. Moses. This apparatus consists of a turntable which revolves around the light source (Hanovia L679A 450-watt medium pressure mercury lamp) contained in a quartz cooling well held in the center. Four sets of glass filters can be placed around the quartz well. The turntable provides room for thirty sample tubes, all held in equivalent positions. The windows through which the light passes to each sample were very carefully machined so that their areas vary less than 0.5%.

For 2537 Å excitation, a bank of four General Electric T-6 low pressure mercury germicidal lamps was employed. The lamps are mounted in an aluminum case. Mounted on the outside of the case in front of a window is a Beckman u.v.-cell holder. Glass filters or cells containing filter solution can be placed inside the case in front of the window.

Various filters and filter combinations were employed. Their transmission curves are shown in Figures III and IV. Interference filters (Baird Atomics) with band pass maxima at 2870 Å (A in Figure III) and at 3000 Å (B in Figure III) were used only in the case of naphthalene. The most extensively used filter system consisted of a Corning C.S. 7-54 glass filter, 2.5 cm of 0.455 M $NiCl_2$ in water, 2.0 cm of 0.0005 M $K_2CrO_4$ in water, and 2.0 cm of 0.0049 M potassium biphthalate in water (quartz solution holders in all cases). Curve C in Figure III shows the transmission properties of this filter train. When this filter train is used in conjunction with the Westinghouse SAH-800-c lamp, 92% of the quanta that pass through have wavelengths near 3130 Å , the remaining 8% have wavelengths near 3340 Å. No 3022 Å excitation is passed. The spectral distribution of the light was determined by determining the relative rates for the benzophenone sensitized isomerization of *cis*-piperylene using the filter train with and without a Corning C.S. 1-51 glass filter (D in Figure III) added. From the relative rates and the transmission characteristics of the 1-51 filter at 3130 and 3340 Å, the relative amounts of excitation at those wavelengths is easily determined. A combination of Corning C.S. 7-37 and 0-52 glass filters (E in Figure III) was employed to isolate the group of mercury lines near 3660 Å. The spectrum of the light from the Westinghouse SAH-800-c lamp passed through these filters is shown in Figure V. This spectrum

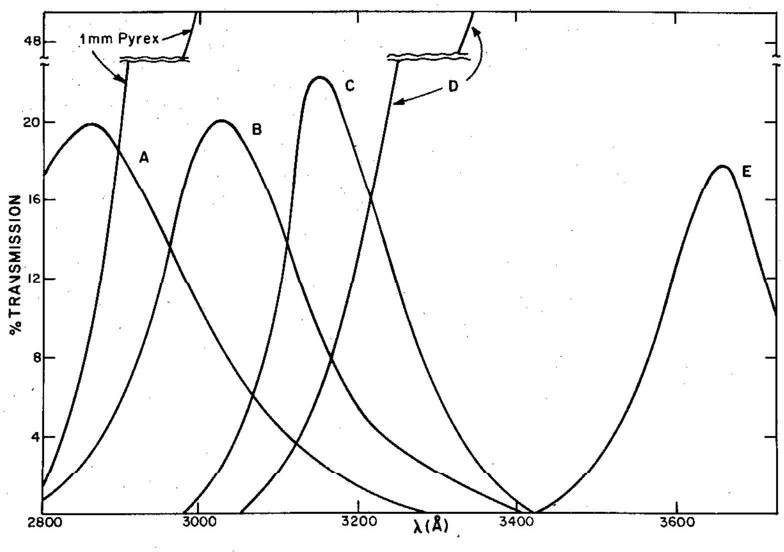

Figure III. Transmission curves for 1 mm-pyrex; the "2870 Å" interference filter (A); the "3000 Å" interference filter (B); the "3130 Å" filter train (C); a Corning C.S. 1-51 glass filter (D); and Corning C.S. 0-52, C.S. 7-37 glass filters (E).

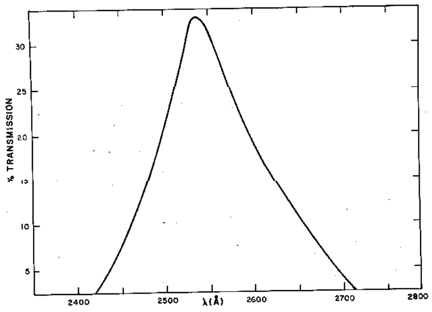

Figure IV. Transmission curve for a 2.5 cm path of 2.4 x $10^{-4}$ M p-nitrophenol in water.

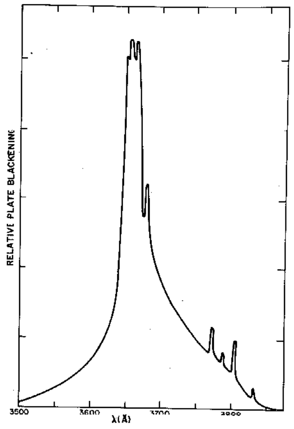

Figure V. Densitometer tracing of a photograph of the emission from a Westinghouse SAH-800 c mercury lamp filtered through Corning C.S. 7-37 & 0-52 glass filters.

was recorded spectrographically using a 1/2-meter prism spectrograph. To isolate the 2537 Å line from the emission of the germicidal lamps, 2.5 cm of 2.4 x $10^{-4}$ M p-nitrophenol in water was employed (Figure IV).

The following is the code for source and filter combinations for use with Table VI.

| Source | Description | |
|---|---|---|
| | Apparatus | Filters |
| 1 | optical bench | Corning C.S. 0-52 and 7-37 |
| 2 | optical bench | "3130 Å" filter train |
| 3 | optical bench | "3000 Å" interference filter |
| 4 | optical bench | "2870 Å" interference filter |
| 5 | "merry-go-round" | Corning C.S. 0-52 and 7-37 |
| 6 | germicidal lamps | p-nitrophenol solution |

When using the optical bench, a run consisted of irradiating one sample tube containing benzophenone as sensitizer along with three other tubes containing other sensitizers. A second identical set was then irradiated. In general irradiation times were one to four hours and conversions were 1-5%. When using the merry-go-round, four sample tubes containing benzophenone and tubes containing other sensitizers (two each and up to thirty tubes in all) were irradiated simultaneously. Irradiation times were two to four hours.

Analyses:

The vapor phase chromatographic technique was used to analyze all the cis-trans-olefin mixtures. A Loenco Model 15B fractometer equipped with a hydrogen flame ionization detector was used throughout this work. This detection system allows for accurate determination of the extent of isomerization even for conversions as low as 0.5% in samples where the total olefin concentration is 0.05 M. A Brown recorder (1 sec response) equipped with a disc integrator was used to record the chromatograms. The areas under the olefin peaks were determined from the disc integrator deflection. Each sample was analyzed twice. The olefin isomer ratios usually agreed within 3-5%.

The chromatographic columns and conditions used to effect separation of the various olefin pairs were as follows. The piperylenes were separated on a 20 ft x 1/4 in column packed with 15% 1,2-bis[2-cyanoethoxy]ethane on 20 M Chromosorb (45-60 mesh) and maintained at room temperature. The β-methylstyrenes were separated on a 7 ft x 1/4 in column packed with 20% γ-methyl-γ-nitropimelonitrile on Chromosorb W (60-80 mesh) and maintained at 120°. The α-methylstyrenes were separated on a 7 ft x 1/4 in column packed with 20% Apiezon L on Chromosorb W (60-80 mesh) and maintained at 250°. In the case of the α-methylstilbene analysis, it was found that certain of the sensitizers had comparable retention times and were eluted with the olefins. It was necessary, therefore, to remove the sensitizer before the analysis. Since all the cases involved sensitizers which were carbonyl compounds, this was easily accomplished by first passing the mixture through a small column (10 in x 1/2 in) dry-packed with about 10 g. alumina. An additional amount (8-15 ml) of benzene was required to elute all of the olefins. None of the carbonyl compounds were eluted. The eluent was concentrated to about one-third its volume by slow evaporation in an air stream. It was shown previously ( 50 ) that this separation technique does not alter the olefin-isomer ratio.

All measured conversions were corrected for back reaction by using equation 26.

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# PART II

# INTRAMOLECULAR ELECTRONIC ENERGY TRANSFER BETWEEN NON-CONJUGATED CHROMOPHORES IN SOME MODEL COMPOUNDS

# INTRODUCTION

There has been great interest and activity in the study and application of intermolecular electronic energy transfer in the last decade and promises of even greater activity are evident. The gross characteristics of various modes for transfer of both singlet and triplet excitation have been documented, and for certain cases, quantitative theories have been worked out in detail. On the other hand, one important area, the study of intramolecular electronic energy transfer between chemically different non-conjugated chromophores has received relatively little attention. This is an interesting area for a number of reasons. One is that molecular dimensions are well within the limits where some of the simple theoretical treatments break down. Altogether new transfer processes might operate at such close approach of donor and acceptor. Furthermore, the molecular "bridge" connecting the chromophores could act as a "pipeline" for excitation transfer. The study of excitation transfer between chromophores having known fixed spatial dispositions relative to each other is also possible. Finally, these studies would find immediate application to the study of radiation damage in biologically important systems such as the nucleic acids, which are composed of large numbers of non-conjugated chromophores.

The remainder of this introduction will be concerned with a brief review of what is known about electronic energy transfer mechanisms and a review of the work done on intramolecular electronic excitation migration.

## Mechanisms of Electronic Energy Transfer

Source material for the following brief discussion of electronic excitation transfer mechanisms can be found in the excellent reviews of Dexter (1), Förster (2), Livingston (3), Porter and Wilkinson (4), and Ermolaev (5), and references therein. The following discussion will be based on three general mechanistic types--the radiative or "trivial" type, radiationless processes involving exchange interactions through overlap of donor and acceptor electron clouds, and radiationless exciton transfer.

## The Trivial Process

The "trivial" process involves the possibility of reabsorption of donor emission. This radiative process can occur over large distances, since the probability that a molecule A reabsorbs the light emitted by another molecule B at a distance R varies as a function of $R^{-2}$. The situation is summarized in equations 1-3, where the asterisks denote excited molecules. Only energies corresponding to that part of the emission spectrum of D that overlaps with the absorption spectrum of A can be transferred. Gaviola and

$$D + h\nu \rightarrow D^{*} \tag{1}$$

$$D^{*} \rightarrow D + h\nu' \tag{2}$$

$$h\nu' + A \rightarrow A^{*} \tag{3}$$

Pringsheim (6) have shown that this process contributes little when D and A are similar molecules due to the usually small overlap of emission and absorption spectra in this case. Consequently, the process was termed "trivial." Energy transfer by the trivial process is characterized by the invariance of the donor emission lifetime, the change in the donor emission spectrum, and the lack of dependence upon the viscosity of the medium.

## Transfer Requiring Overlap Interaction

Transfer due to overlap of donor and acceptor electron clouds is very short-range due to the exponential fall-off of electron wavefunctions at the boundaries of a molecule. In the case of low-lying energy states of molecular crystals, intermolecular overlap is not usually significant. In some cases where significant overlap occurs in the excited states, photoconduction bands are formed and the crystal is photoconducting. When photoconduction bands are excited, the excitation energy is delocalized due to electron mobility. For such a strong interaction as overlap interaction, collective excitation is the best description of the excitation process; therefore the idea of transfer of energy is meaningless. In inorganic phosphors, the dominant excitation mechanism involves excitation of a conduction band of the crystal.

Dexter (1) treated the case of excitation transfer by the exchange interaction involving a single donor and acceptor. According to Dexter, not only has spin momentum to be conserved for an exchange mechanism, but $X_D^*$ must equal $X_A^*$ and $X_D = X_A$, where $X_D^*$ and $X_A^*$ refer to the multiplicity of the donor and acceptor in their excited states, and $X_D$ and $X_A$ to the multiplicities in their ground states. The probability for transfer is given by equation 4,

$$P_{DA} = \frac{2\pi}{\hbar} Z^2 \int f_D(E)\, F_A(E)\, dE \tag{4}$$

where $\int f_D(E)\, F_A(E)\, dE$ is a type of overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor, and $Z^2$, which has the dimensions of energy squared, cannot be directly related to optical experiments. The transfer probability falls off exponentially with distance.

The experimental results for triplet energy transfer (4, 5) are perfectly consistent with an exchange mechanism of the Dexter type. The excellent studies by Terinen and Ermolaev (5) of triplet transfer between various donor-acceptor pairs (sensitized phosphorescence) dissolved in glassy solution at low temperatures first demonstrated the requirement of close approach of donor and acceptor. The distance between the centers of the donor and acceptor molecules within which transfer takes place was determined to be 10-15 Å for 23 donor-acceptor pairs. In fluid solution (7), intermolecular distances of this magnitude are encountered in collisions. The rate of triplet energy transfer in fluid solution would not be expected to exceed that calculated for diffusion-controlled encounters between molecules which have normal cross sections. This is what is observed (4). For those systems which have the triplet level of the donor at least 1000 $cm^{-1}$ above that of the acceptor, the transfer rate is diffusion controlled. There are no indications that the quenching efficiency decreases as the separation increases, but as it decreases the transfer occurs at a rate considerably less than the encounter rate. When the triplet level of the donor is below that of the acceptor, no transfer is observed.* No dependence upon the probabilities of the radiative singlet-triplet transitions in the donor and acceptor are observed. Finally, collisional transfer of any kind is characterized by its decrease with increasing viscosity if diffusion-controlled, and by the decrease of the lifetime of the excited state of the donor. However, the

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* "Endothermic" transfer has been observed to be quite efficient in systems where the acceptor is a flexible molecule and the transfer involves nuclear motion in the acceptor, i.e. a non-vertical transition (8).

absorption and emission spectra of the donor and acceptor remain unchanged.

## Exciton Transfer

The longer-range electronic energy transfer considered in this section is that due to exciton interaction. This type has been given various names, such as resonance transfer, inductive resonance, and exciton transfer. All these processes, however, are based on similar mechanisms in which energy transfer results from the weak intermolecular interaction between donor and acceptor. It is this weak interaction which allows the energy coupling between excited and unexcited molecules. The extent of such coupling depends mostly upon the intermolecular distance and orientation and the radiative probabilities of the transitions under consideration, as well as their relative energies. Different cases arise corresponding to various degrees of coupling, and they all may be considered as different cases of the exciton mechanism for electronic energy transfer (9). The reason is that the term responsible for energy transfer corresponds to the energy exchange term in the exciton treatment (10).

The detailed mechanism of energy transfer depends on the magnitude of the intermolecular electronic interaction relative to intramolecular vibrational-electronic coupling and vibronic coupling with the environment. Simpson and Peterson (11) proposed criteria in this regard for the cases of crystalline molecular solids or other molecular aggregates. For their strong-coupling exciton case, they propose the criterion $2\beta/\Delta\epsilon >> 1$, where $2\beta$ is the exciton band width, and $\Delta\epsilon$ is the Franck-Condon band width of the corresponding electronic transition in the individual molecular unit. For the weak coupling criterion, Simpson and Peterson propose the converse inequality, $2\beta/\Delta\epsilon << 1$. Strong-coupling leads to a band shift for the excition states of the aggregate which is larger than the total electronic band width for the transition in the individual molecule. Davydov (12) gives criteria based on different premises. He classified free excitons as those for which the lifetime of a locally excited state ($t = h/2\Delta\beta$) is much shorter than the lattice relaxation time (time for the lattice to re-equilibrate as a result of changes in intermolecular forces caused by excitation). Localized excitons correspond to the converse inequality. In this case, the transfer rate is limited by the lattice relaxation. These two limits roughly correspond to the strong and weak coupling cases of Simpson and Peterson.

Förster (2) proposed a modified view of the Simpson-Peterson criteria. He proposed that Simpson and Peterson's criteria be reclassified as "strong-coupling" and "medium-coupling" and that "weak-coupling" be reserved for his vibrational-relaxation resonance case where $\beta/\Delta\varepsilon' << 1$, where $\beta$ is the interaction energy and $\Delta\varepsilon'$ is the individual vibronic band width. However, there is a serious discontinuity between the Davydov, Simpson-Peterson model and Förster's model. The exciton (Davydov) model is based essentially on a first-order perturbation treatment with an inverse-cube dependence on the distance between interacting excited-state transition dipoles. Förster's model, which yields results (experimentally documented) of the form, familiar in second-order perturbation theory, which depends on the inverse sixth power of the distance between interacting dipoles.

The rates of excitation transfer for dipole-dipole interaction* based on these three cases are given by equations 5, 6, and 7, where

Strong-coupling
(Simpson-Peterson)

$$P \sim \frac{f}{r^3}\,\theta(\theta) \qquad (5)$$

Weak-coupling
(Simpson-Peterson)

$$P \sim \left(\frac{f}{r^3}\,\theta\right) \sum_{v,v'} g^*_v g_{v'} S^2_{vv'} \qquad (6)$$

Very weak
(Förster)

$$P \sim \left(\frac{f}{r^3}\,\theta\right)^2 \frac{\sum_{v,v'} g^*_v g_{v'} S^4_{vv'}}{\Delta\varepsilon'} \qquad (7)$$

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* The intermolecular interaction should be expressed by potential terms of coulomb type. This leads to intractable mathematics, and so the intermolecular coulomb potential is replaced by a multipole expansion, and only the dipole-dipole term is used as an approximation.

f is the total oscillator strength of the electronic transition, $\theta(\theta)$ is a geometrical function for the angular dependence of the interaction, and r is the distance between the interacting centers. In the weak-coupling case, a vibrational overlap integral (summing over the vibrational levels v' and v of the non-excited and excited molecules, respectively) is present . It should be noted that, although the strong-coupling exciton (transfer rate $> 10^{12}$ sec) is often thought of as an excitation exchange mechanism for identical, strongly absorbing molecules in the solid state, nevertheless it also may apply in the intermediate-coupling or weak-coupling case to dissimilar molecules with fairly close lowest excited energy levels, or to molecules dispersed in a medium with intermolecular distances to 100 Å. The mechanism introduced by Förster (2) is widely thought to be the only long-range mechanism available from theory. In his model, the transfer is evidently not so long-range as the exciton models provide. However, for transfer between dissimilar molecules, the Förster mechanism is probably the dominant one at large distances. A detailed treatment (2) for this case yields a transfer probability given by equation 8, where $\eta$ is the refractive

$$P_{DA} = \frac{0.113\,\theta}{\eta^4 N r^6} \int f_D(\bar{\nu})\, \epsilon_A(\nu)\, \frac{d\bar{\nu}}{\bar{\nu}^2} \qquad (8)$$

index of the solvent, N is Avogadro's number, r is the distance

## Exciton Transfer

| Theoretical Model | Coupling Criteria | Experimental Model | Characteristics |
|---|---|---|---|
| Exciton Model (Davydov) | strong<br>$\frac{2\beta}{\Delta\varepsilon} >> 1$ | free exciton | collective excitation, band shift transfer rate $> 10^{12}$ sec$^{-1}$<br>$\propto 1/r^3$ |
| | weak<br>$\frac{2\beta}{\Delta\varepsilon} << 1$ | localized exciton | localized excitation<br>stepwise transfer (identical units)<br>transfer rate $\sim 10^{12}$ sec$^{-1}$<br>$\propto 1/r^3$ |
| Förster | very weak<br>$\frac{\beta}{\Delta\varepsilon'} << 1$ | vibrational-relaxation resonance transfer | stepwise transfer (dissimilar units)<br>transfer rate $< 10^{11}$ sec$^{-1}$<br>$\propto 1/r^6$ |

FIGURE I

between the interacting dipoles, $\theta$ is the orientation factor, and $\int f_D(\bar{\nu})\ \epsilon_A(\bar{\nu})$ is an "overlap" integral involving the emission spectrum of the donor and absorption spectrum of the acceptor. If $f_D$ and/or especially $\epsilon_A$ are small, then close approach is required between donor and acceptor. If the transitions in the donor and acceptor are both strong, large transfer distances are predicted. Cases of transfer over distances of nearly 100 Å have been documented (2, 13). However, the dependence upon distance ($1/r^3$ or $1/r^6$ or some other function) has not been determined chiefly due to experimental difficulties.

Long-range exciton transfer is characterized by a decrease in the donor emission lifetime, a non-dependence upon medium viscosity, and no change in the absorption spectra of the donor and acceptor,

A very important unifying contribution to the understanding of both excitation transfer and relaxation, with regard to a physically satisfying picture of the mathematical limits used as criteria for differentiating among the various transfer mechanisms, is given by Robinson and Frosch (14). Finally, it is important to mention a point which is emphasized by Robinson and Frosch (14). In molecular crystals or for any close approach of donor and acceptor, higher terms in the multipole expansion or second-order perturbation contributions may exceed the dipole-dipole interaction.

## Intramolecular Electronic Energy Transfer

Any radiationless combination involving two excited states within a molecule may be considered an example of intramolecular electronic energy transfer. Thus, within this definition, internal conversion and intersystem crossing (7) are types of intramolecular excitation transfer (14). It becomes immediately evident that the various types of intramolecular transfer cannot be usefully categorized on the basis of strength of coupling or rate of transfer, but are most usefully classified with respect to the locale of the excitation. Thus, two main classifications arise; transfer within the same chromophore and excitation transfer between two chromophores. The latter is usefully split into two subgroups: excitation transfer between conjugated chromophores and transfer between non-conjugated chromophores.

Excitation transfer within the same chromophore includes almost all the cases of internal conversion and intersystem crossing between excited states. The reader is referred to Part I of this thesis and references therein for a review of these topics.

The absorption spectrum of a molecule that contains two chromophores which are not conjugated is for the most part the same as the combined spectra of the two chromophores alone in separate molecules. The long-range interactions between the excited states of the chromophores give rise to only small (but important) spectral changes. If, however, the chromophores are conjugated, the absorption spectrum usually differs from the combined spectra of the two chromophores alone in separate molecules, because of the overlapping of the wave functions which delocalize the electrons (resonance), and because of exciton delocalization which is not overlap dependent. Only the latter leads to spectral changes in the case of non-conjugated chromophores. For conjugated chromophores it is usually difficult to differentiate overlap independent effects from resonance effects. On the other hand, some molecules containing conjugated dissimilar chromophores exhibit absorption spectra which have long-wavelength regions which resemble very closely the combined spectra of the chromophores alone in different molecules.

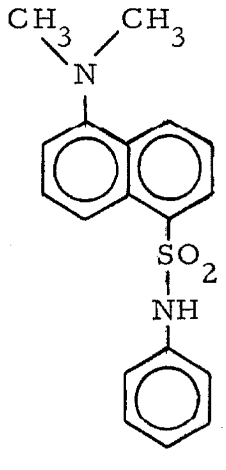
Ermolaev and Terinen (15) noted that the long-wavelength region of the absorption spectrum of 4-benzoylbiphenyl is very much like that of benzophenone. They interpret this to mean that the $n \rightarrow \pi^*$ singlet state is of the same energy and is the lowest excited singlet state in both compounds. This must mean that the excitation is fairly well localized to the carbonyl group. The lowest triplet state of biphenyl lies lower than that of benzophenone. Ermolaev and Terinen found that the phosphorescent emission from

4-benzoylbiphenyl is very similar to that of biphenyl. They interpreted this result as an example of intramolecular energy transfer from the carbonyl $n \rightarrow \pi^*$ triplet to the lowest $(\pi \rightarrow \pi^*)$ triplet state of the biphenyl system. There is no proof, however, that the excitation was transferred via the $n \rightarrow \pi^*$ triplet, i.e. other paths from the $n \rightarrow \pi^*$ singlet to the biphenyl lowest triplet may operate.

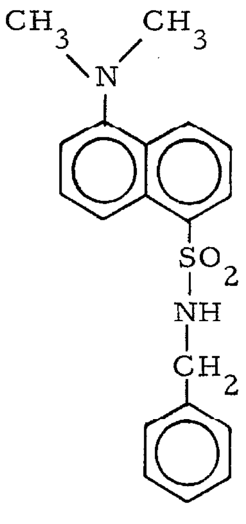
Certain chelates of the rare-earth elements offer more straightforward examples of excitation transfer between conjugated chromophores. Crosby (16) first noted that excitation of the organic ligands leads to emission characteristic of the metal ion if the lowest triplet state of the ligand lies above the emitting state of the ion. If no ion excited state lies below the ligand triplet, phosphorescent emission from the ligand is observed. Recently Bhaumik and El-Sayed (17) showed proof for the Crosby model. They were able to find quenchers with lowest triplet levels in between those of the ion and ligand for certain europium and terbium chelates. They showed unambiguously that intermolecular quenching of the ligand triplet interrupted excitation transfer to the ion. Thus, the mechanism for ion excitation is by transfer of triplet excitation from the ligand. The small amount (~10%) of residual ion emission at high quencher concentration was attributed to singlet excitation transfer. From the quenching experiments, a lower limit of $10^9$ $sec^{-1}$ was determined for triplet excitation transfer from the ligand to the ion. Bhaumik and El-Sayed claim this rate is consistent with an exchange interaction mechanism.

Whereas the dominant transfer mechanism for excitation transfer would be expected to be the exchange mechanism, the case of transfer between non-conjugated chromophores offers the possibility of an exciton mechanism or an exchange mechanism involving the molecular "bridge." A few studies of intramolecular excitation transfer between non-conjugated chromophores have been reported in the literature. These are discussed below.

Weber and Teale (18) measured the action spectrum for fluorescence from 1-dimethylaminonaphthalene-5-(N-phenyl)sulphonamide (I) and 1-dimethylaminonaphthalene-5-(N-benzyl)sulphonamide (II). The action spectrum for II followed its absorption spectrum exactly even in the region where some of the exciting light was



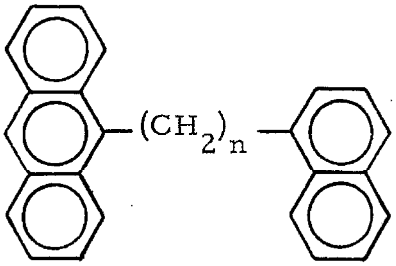
(I)



(II)

absorbed by the phenyl group. Evidently, efficient transfer of signlet excitation from the phenyl group to the naphthalene group takes place. For I, however, the action spectrum drops off significantly in the region where aniline absorbs. In this case, excitation transfer cannot compete with other deactivation processes of the aniline singlet state. Weber and Teale attribute (18) the transfer in II to an exciton mechanism. Weber (19) reported that efficient singlet excitation transfer takes place between the adenine and N-alkylnicotinamide moieties in dehydro diphosphopyridine nucleotide. There is some evidence that efficient migration of triplet excitation takes place in the nucleic acids (20).

The most extensive study of a case of intramolecular excitation transfer between non-conjugated chromophores reported in the literature is that by Schnepp and Levy (21) of singlet excitation transfer from the naphthalene group to the anthracene group in the homologous III-V. The absorption spectra of the compounds are



III n = 1
IV n = 2
V n = 3

virtually superimposable upon the absorption spectrum of an equimolar mixture of 9-methylanthracene and 1-methylnaphthalene.* Schnepp and Levy showed that in glassy solution at 77°K only anthracene fluorescence is observed from III, IV, and V, even if the compounds are excited at a wavelength where the naphthalene moiety absorbs most of the light. The transfer is equally efficient in all three cases, 30 ± 13% of the quanta absorbed by the naphthalene group being transferred. Using an equimolar mixture of 1-methylnaphthalene and 9-methylanthracene at concentrations similar to those of III-V, they showed that no intermolecular transfer takes place. The investigators pointed out that lengthening the "bridge" from one to three methylene groups does not significantly lengthen the distance between the chromophores because of the flexibility of the methylene chain. Thus, it is not surprising that the same efficiency was attained in each case. They considered an exciton mechanism for the transfer and felt that the "bridge" played no part. Naphthalene phosphorescence was not observed either, so that transfer of triplet excitation to the anthracene moiety must also take place. This interesting system will be discussed again in a later section.

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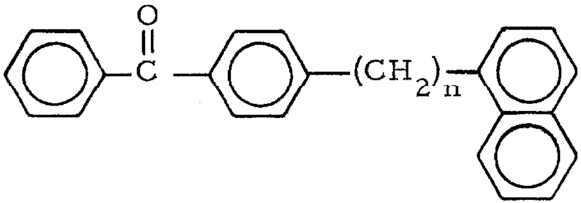
* The lowest singlet state of naphthalene lies higher than that of anthracene. The same situation is found for the lowest triplet states.

## The Leermakers' Compounds

The remainder of this part describes a study of intramolecular excitation transfer in the Leermakers' Compounds LI, LII, and LIII. The compounds consist of a benzophenone moiety attached at its 4-position to the 1-position of a naphthalene ring by a methylene bridge. The absorption spectra of the compounds resemble very closely the absorption spectrum of an equimolar mixture of 4-methylbenzophenone and 1-methylnaphthalene. The name Leermakers' Compounds derives from Professor P. A. Leermakers, who suggested this problem. The compounds were synthesized in Professor Leermakers' laboratory by Mr. Gary Byers.



LI n = 1
LII n = 2
LIII n = 3

The features of the Leermakers' Compounds which make them especially interesting from the viewpoint of intramolecular energy transfer can be seen by considering the positions of the lowest excited singlet and triplet levels of benzophenone and naphthalene (Figure II). The lowest excited singlet level of benzophenone ($B^S$) lies about 3000 $cm^{-1}$ below that of naphthalene ($N^S$), but the lowest

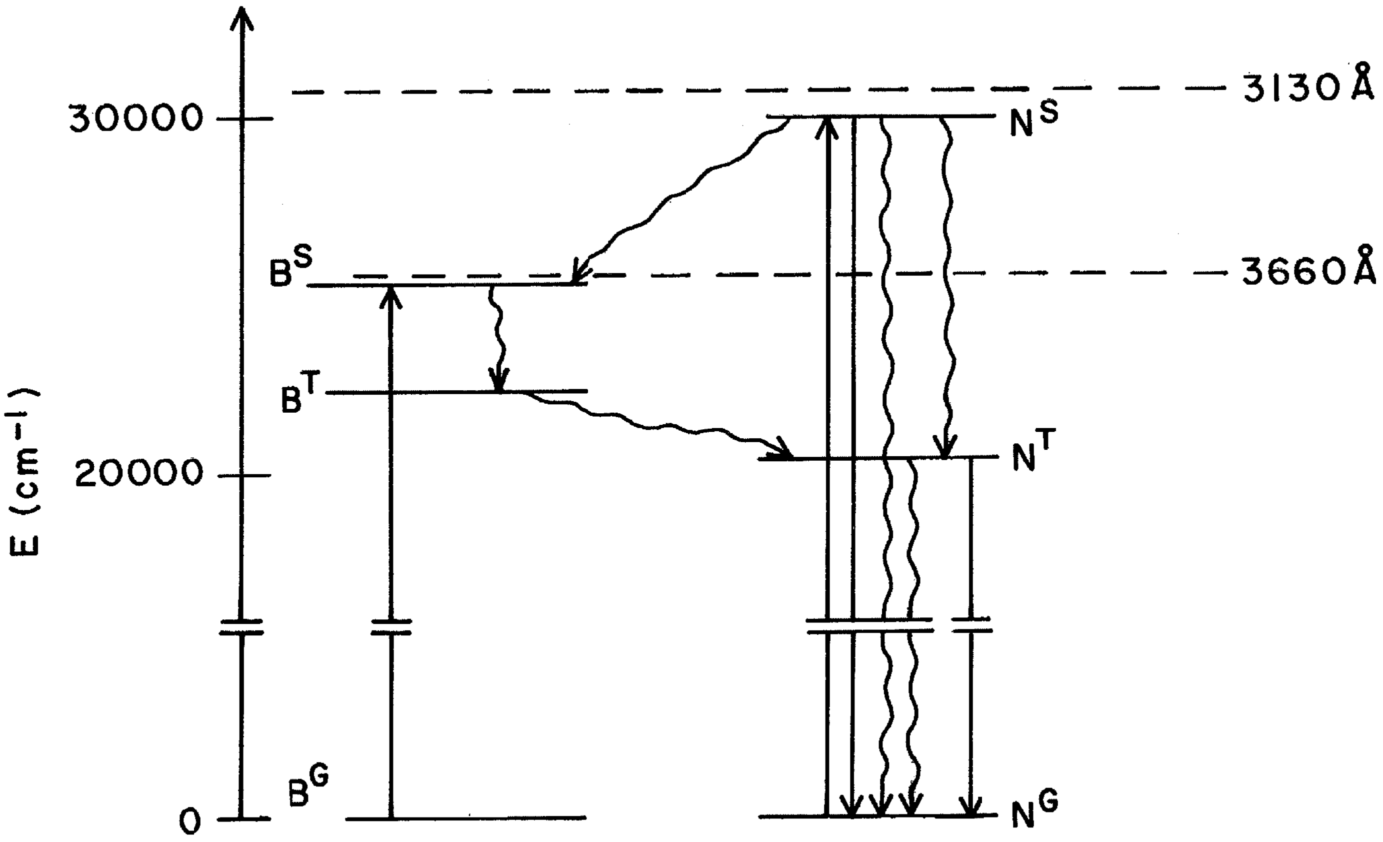


FIGURE II

Excitation energies to the first excited singlet (S) and lowest triplet (T) states from ground states (G) of benzophenone (B) and naphthalene (N) moietics in the Leermakers' Compounds. Possible radiative transitions are represented by straight arrows, radiationless transitions by wavy arrows.

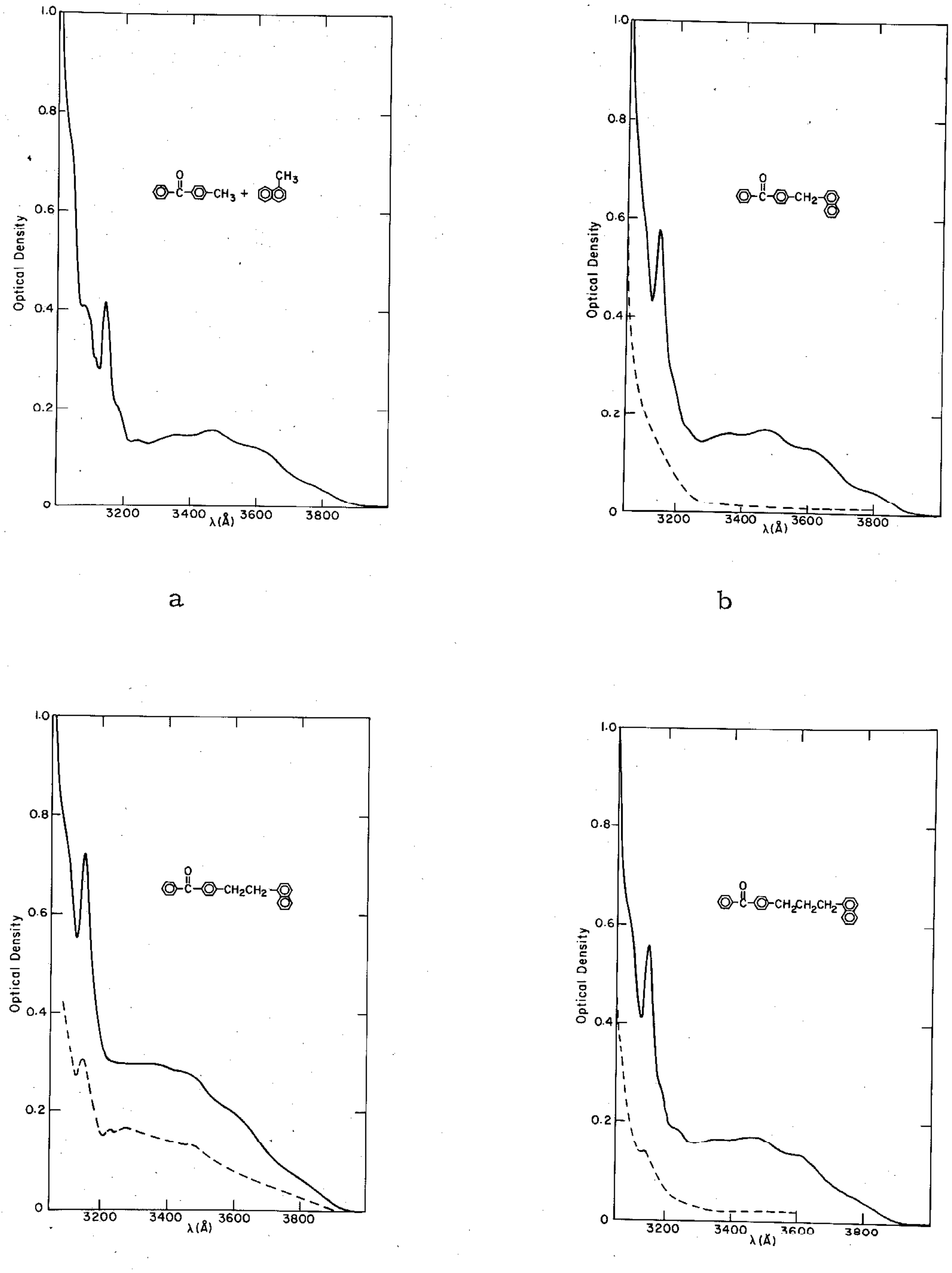
triplet level of benzophenone ($B^T$) lies about 3000 $cm^{-1}$ higher than that of naphthalene ($N^T$). It would be possible on the basis of energetics to have singlet energy transfer from naphthalene to benzophenone and triplet energy transfer from benzophenone to naphthalene. Intermolecular triplet transfer from benzophenone to naphthalene was the first documented case of its kind (22). Naphthalene does not absorb light of wavelengths greater than 3200 Å , while the $n \rightarrow \pi^*$ transition in benzophenone is centered near 3500 Å. Using the group of mercury lines near 3660 Å, it is possible to excite only the benzophenone moieties in the Leermakers' Compounds. The ratio of the extinction coefficients of naphthalene and benzophenone at 3130 Å is about 4. Using the group of mercury lines centered at 3130 Å, it is possible to preferentially excite the naphthalene groups in the Leermakers' Compounds. Thus, from an experimental point of view, the compounds are nearly ideal.

# EXPERIMENTS AND RESULTS

Five different kinds of measurements were obtained in order to elucidate the modes and efficiencies of excitation transfers in the Leermakers' Compounds. These included the determination of absorption spectra, and emission spectra, the measurement of emission lifetimes, the characterization of the compounds as triplet sensitizers in the isomerization of olefins, and measurements of the yields of quenchable triplets. The last four listed measurements were obtained with excitation originally localized on each chromophore. 1-Methylnaphthalene, 4-methylbenzophenone, and equimolar mixtures of the two served as "standards."

## Absorption Spectra

An equimolar ($10^{-3}$ M) mixture of 1-methylnaphthalene and 4-methylbenzophenone in cyclohexane exhibits an absorption spectrum (Figure IIIa) exactly equal to the sum of the absorption spectra of 1-methylnaphthalene and 4-methylbenzophenone recorded above. Figures IIIb, c, and d show the absorption spectra of LI, LII, and LIII, respectively. Difference spectra computed by subtracting the spectrum of the equimolar mixture of 1-methylnaphthalene and 4-methylbenzophenone from each of the other spectra are also shown (dashed lines).



a b c d

Absorption Spectra
(Compounds were $10^{-3}$ M dissolved in cyclohexane. Difference spectra shown in dashed lines.)
FIGURE III

## Emission Spectra

Emission spectra were recorded spectrophotometrically using a scanning grating monochrometer. Exciting light of 3130 or 3660 Å wavelength could be employed. The samples were dissolved in EPA (ether:isopentane:ethylalcohol 5:5:2) and formed clear glasses at 77°K, at which temperature all spectra were recorded.

The only emission detected from an equimolar ($5 \times 10^{-3}$ M) mixture of 1-methylnaphthalene and 4-methylbenzophenone under excitation with 3660 Å light was phosphorescent emission from 4-methylbenzophenone (Figure IV). This result indicates that at the concentrations employed, there is little, if any, intermolecular transfer of triplet excitation such as that observed by Terinen and Ermolaev (5, 22) for more concentrated mixtures of benzophenone and naphthalene under similar conditions. The phosphorescence spectra of LI, LII, or LIII, however, are almost identical to that of 1-methylnaphthalene even when only the benzophenone chromophore is excited. No emission characteristic of 4-methylbenzophenone was observed from LI, LII, or LIII under conditions where 0.1% emission from the benzophenone moiety could have been detected. Figure IV shows the phosphorescence spectrum of LI along with that of 1-methylnaphthalene. Table I lists some band maxima from the phosphorescence spectra of LI, LII, LIII, and 1-methylnaphthalene.

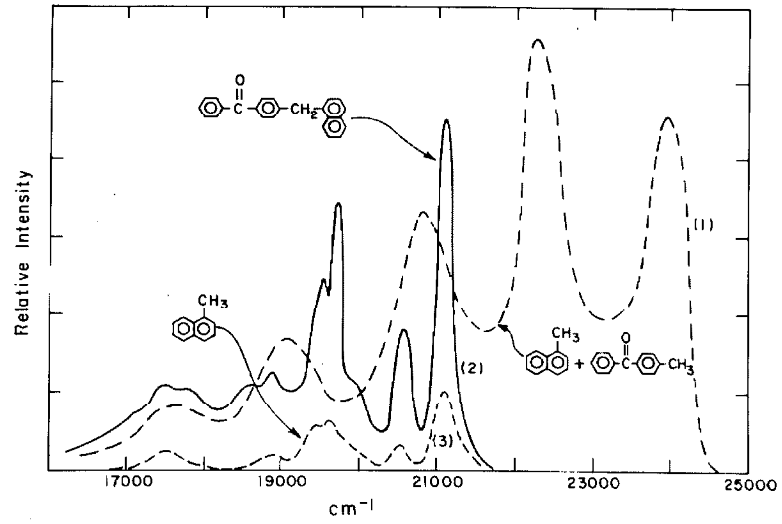


Figure IV. Phosphorescence spectra in EPA at 77°K; exciting light 3660 Å for (1) and (2), 3130 Å for (3); room temperature concentrations 5 x $10^{-3}$ M in all cases; not corrected for instrument spectral sensitivity.

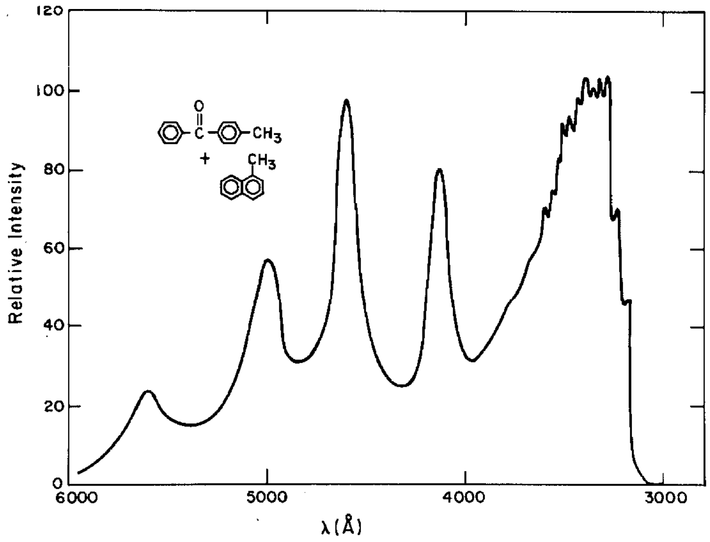


Figure V. Total emission spectrum of an equimolar ($10^{-3}$M) mixture of 1-methylnaphthalene and 4-methylbenzophenone in EPA at 77°K; 3130 Å exciting light; not corrected for instrument spectral sensitivity.

## TABLE I

### Phosphorescence Band Maxima[a] ($cm^{-1}$)

(Samples in EPA at 77°K)

| 1-Methyl-naphthalene | LI | LII | LIII | LI-alcohol |
|---|---|---|---|---|
| 21,044 | 21,097 | 21,008 | 21,008 | 21,044 |
| 20,534 | 20,584 | 20,495 | 20,522 | 20,534 |
| 19,635 | 19,708 | 19,606 | 19,635 | 19,635 |
| 19,500 | 19,547 | 19,464 | 19,483 | 19,500 |

a. Accuracy ± 25 $cm^{-1}$

The total emission spectrum of an equimolar ($10^{-3}$ M) mixture of 1-methylnaphthalene and 4-methylbenzophenone using 3130 Å excitation is shown in Figure V. At this wavelength, the ratio of the number of quanta absorbed by the 1-methylnaphthalene to that absorbed by the 4-methylbenzophenone is about 4:1. But since the quantum yield of phosphorescence from 1-methylnaphthalene is very low (~.05) and that of benzophenone is very high (probably >0.9)(7), the phosphorescent emission from the 4-methylbenzophenone dominates the long-wavelength region. The short-wavelength region of the spectrum contains the fluorescence spectrum of 1-methylnaphthalene. The slight difference between the fluorescence spectrum of the 1-methylnaphthalene in the mixture (Figure V) and that of 1-methylnaphthalene alone (Figure VI) is attributed to a small amount of reabsorption ("trivial" transfer) by the 4-methylbenzophenone. A

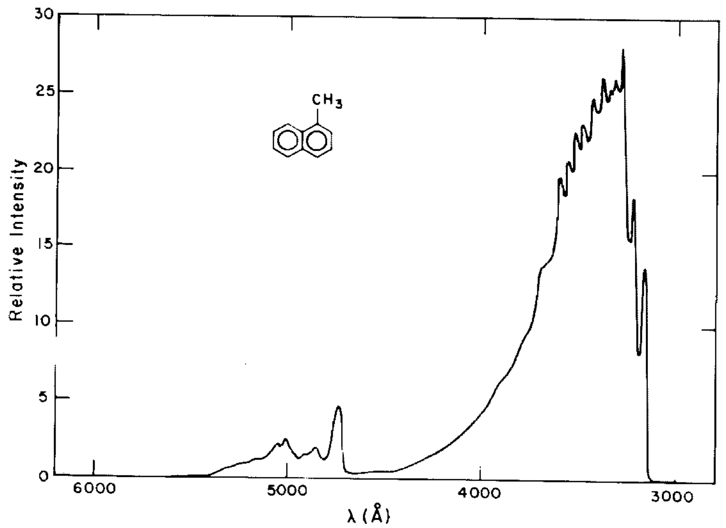


Figure VI. Total emission spectrum of 1-methylnaphthalene ($10^{-3}$ M) in EPA at 77°K; 3130 Å exciting light; not corrected for instrument spectral sensitivity.

calculation of the maximum amount of reabsorption expected (considering concentration, sample size, geometry of the system, etc.) gave between zero and ten per cent, depending upon the wavelength of the 1-methylnaphthalene fluorescence. A discussion of the importance of intermolecular long-range exciton transfer between naphthalene and benzophenone at these concentrations is postponed to a later section.

The total emission spectrum of LI ($10^{-3}$ M) in EPA at 77°K using 3130 Å exciting light is shown in Figure VII. The short-wavelength (3150-4500 Å) emission assigned as fluorescence from the naphthalene chromophore is very weak compared with that

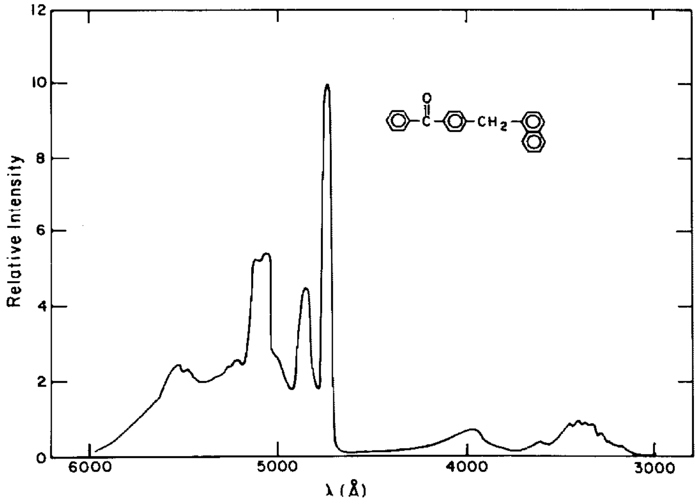


Figure VII. Total emission spectrum of LI ($10^{-3}$ M) in EPA at 77°K; 3130 Å exciting light; not corrected for instrument spectral sensitivity.

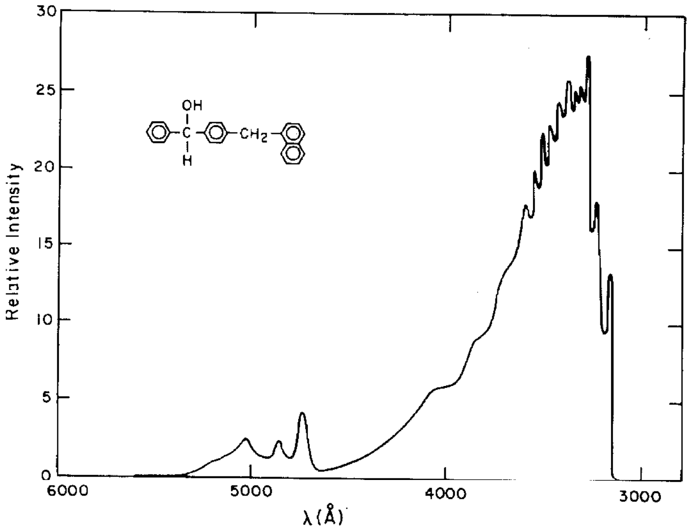
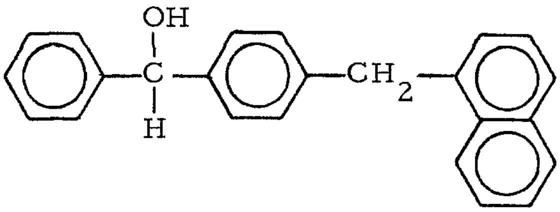


Figure VIII. Total emission spectrum of LI-alcohol ($10^{-3}$ M) in EPA at 77°K; 3130 Å exciting light; not corrected for instrument spectral sensitivity.

recorded from the equimolar mixture of 4-methylbenzophenone and 1-methylnaphthalene (Figure V). Furthermore, the shape of the weak fluorescence spectrum of LI appears to be quite different than that of the fluorescence spectrum of 1-methylnaphthalene (compare Figures V, VI, and VII).

The carbonyl group of LI was reduced with lithium aluminum hydride to give the LI-alcohol. The total emission spectrum of



this compound (Figure VIII) is very similar to that of 1-methylnaphthalene. The naphthalene group fluorescence from samples of LII or LIII (Figures IX and X) is stronger than that from LI. However, the difference in the fluorescence spectra compared to that from 1-methylnaphthalene is much more prominent than in the case of LI. Although the O-O' band positions for the fluorescent emissions from 1-methylnaphthalene and the Leermakers' Compounds are nearly the same (Table II) and all of the compounds exhibit a maximum between 3300 and 3400 Å, the Leermakers' Compounds show another maximum near 4000 Å. The general shapes of the Leermakers' Compounds fluorescence spectra are what would be expected if "trivial" transfer of singlet excitation from naphthalene groups to benzophenone groups

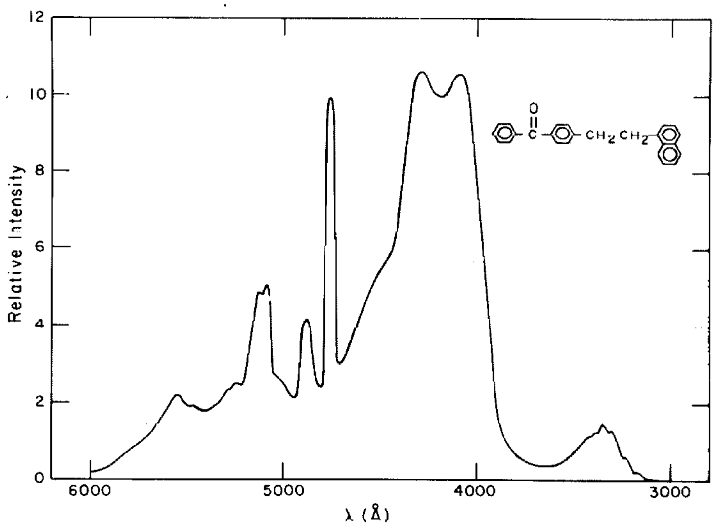


Figure IX. Total emission spectrum of LII ($10^{-3}$ M) in EPA at 77°K; 3130 Å exciting light; not corrected for instrument spectral sensitivity.

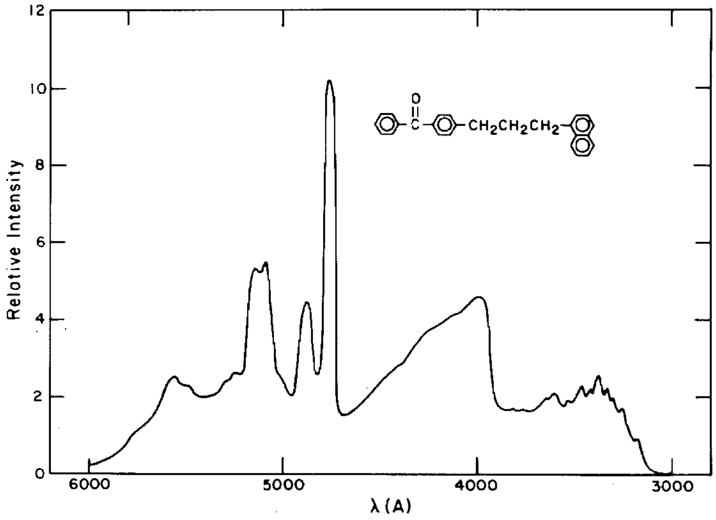


Figure X. Total emission spectrum of LIII ($10^{-3}$ M) in EPA at 77°K; 3130 Å exciting light; not corrected for instrument spectral sensitivity.

TABLE II

Fluorescence O-O' Band Positions [a] ($cm^{-1}$)
($10^{-3}$ M samples; EPA at 77°K; 3130 Å excitation)

| Compound | Position ($cm^{-1}$) |
|---|---|
| 1-Methylnaphthalene | 31,397 |
| LI | 31,348 |
| LII | 31,396 |
| LIII | 31,546 |
| LI-alcohol | 31,505 |

a. Accuracy ± 100 $cm^{-1}$

were occurring. The $n \rightarrow \pi^*$ absorption band of benzophenone extends from 3100 to 3900 Å.

The naphthalene-like phosphorescence from the Leermakers' Compounds is more intense than that from 1-methylnaphthalene or the LI-alcohol. The approximate relative phosphorescence intensities are for 1-methylnaphthalene: LI:LII:LIII, 5:10:7:9.

## Emission Lifetimes

Lifetimes of the phosphorescent emission from the Leermakers' Compounds and 1-methylnaphthalene were determined from decay curves recorded on an oscilloscope. The results are shown in Table III. For a comparison of phosphorescence intensities to be meaningful, the rates of radiative and non-radiative decay of the naphthalene chromophore triplets must be the same (7). Since the

## TABLE III

Phosphorescence Lifetimes
($5 \times 10^{-3}$ M samples; EPA at 77°K)

| Compound | Excitation | $\tau_p$[a] (sec) |
|---|---|---|
| 1-Methylnaphthalene | 3130 | 2.3 |
| LI | " | 2.6 |
| | 3660 | 2.6 |
| LII | 3130 | 2.7 |
| LIII | " | 2.7 |

a. Accuracy ± 10%.

sum of these rates $1/\tau_p$ is nearly the same in all cases, comparison of intensities of phosphorescence is a good indication of the relative numbers of triplets produced upon excitation of the various compounds.

Unfortunately, apparatus for determination of fluorescent lifetimes was unavailable to the author at the time this work was carried out.

### Photosensitized Isomerization of the Piperylenes

The Leermakers' Compounds were used as sensitizers in the photosensitized cis⇄trans isomerization of the piperylenes (1,3-pentadienes).* The isomer ratio at photostationary state is a

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* The reader is referred to Part I of this dissertation and references therein for a discussion of the photosensitized cis⇄trans-isomerization of olefins.

function of the lowest triplet state energy of the sensitizer and so the sensitizer characteristics of the Leermakers' Compounds in this regard would be a chemical method of detecting intramolecular triplet energy transfer. Furthermore, the use of high concentrations of piperylene might allow quenching of the benzophenone moiety triplets in the Leermakers' Compounds demonstrating their existence and yielding information concerning the rates of the triplet excitation transfer. In these experiments, of course, exciting light absorbed only by benzophenone groups is used. The results of these experiments are shown in Table IV. Most of the photostationary state determinations were carried out by Dr. P. A. Leermakers and Mr. G. Byers.

## Yields of Quenchable Triplets

The yields of triplets produced upon excitation of the Leermakers' Compounds, LI-alcohol, and 1-methylnaphthalene were determined by using the triplet counting method described in Part I of this dissertation. cis-Piperylene (0.05 M) was the quencher. The results using exciting light of both 3130 and 3660 Å wavelength are listed in Table V. It was demonstrated in Part I that benzophenone undergoes intersystem crossing with 100 per cent efficiency.

## TABLE IV

### Photostationary Isomer Ratios in the cis⇄trans-Isomerization of the Piperylenes

(Benzene solution; room temperature; 3660 Å excitation)

| Sensitizer | $E_T(\mathrm{cm}^{-1})$[a] | Piperylene conc. (M) | $(t/c)_{\mathrm{p.s.s.}}$[b] |
|---|---|---|---|
| Benzophenone | 23,950 | 0.2 | 1.25 |
| Naphthalene[d] | 21,280 | 0.2 | 2.18[c] |
| 1-Methylnaphthalene[d] | 21,044 | 0.2 | 2.16[c] |
| LI | 21,097 | 0.2 | 2.03[c] |
| | | 0.05 | 2.10 |
| LII | 21,008 | 0.2 | 1.99[c] |
| | | 0.05 | 2.11 |
| LIII | 21,008 | 0.2 | 1.97[c] |
| | | 0.05 | 2.07 |

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a. Lowest triplet level (O-O' band position in phosphorescence spectrum).

b. (trans/cis) at photostationary state; accuracy ±.03.

c. Data of P. A. Leermakers and G. Byers.

d. 3130 Å excitation.

## TABLE V

### Yields of Triplets

(Benzene solution at room temperature; cis-piperylene[b] quencher)

| Sensitizer | Conc. | Excitation: 3130 Å | 3660 Å |
|---|---|---|---|
| Benzophenone | 0.05 | [1.00] | [1.00] |
| 4-Methylbenzophenone | 0.05 | 1.00 | 1.00[c] |
| 1-Methylnaphthalene | 0.0125 | 0.48 | --- |
| LI | 0.05 | | 1.00 |
| | 0.01 | 0.98 | |
| LII | 0.05 | | 0.99 |
| | 0.01 | 0.80 | |
| LIII | 0.05 | | 1.01 |
| | 0.01 | 0.94 | |
| LI-alcohol | 0.0125 | 0.58 | --- |

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a. Relative to benzophenone; yield of triplets upon excitation of benzophenone is 1.00 (7).

b. cis-Piperylene concentration was 0.05 in all cases.

c. Precision is ± 5%.

# DISCUSSION

Several interesting observations concerning intramolecular electronic energy transfer in the Leermakers' Compounds can be made. However, very few conclusions concerning the mechanisms for excitation transfer within these compounds can be drawn from the presently available data. A discussion of the data and interpretations with regard to mechanism follow.

## Absorption Spectra

The absorption spectrum of a molecule containing two chromophores which are far apart and separated by a chain of saturated atoms is essentially the same as that of an equimolar mixture of the two chromophores in separate molecules. This result was confirmed by Ramart-Lucas et al. (23) for several molecules of the type A-$(CH_2)_n$-B, where A and B are phenyl, carbonyl, carboxyl and vinyl. The small but important spectral changes are due chiefly to long-range exciton interaction between the excited states of the chromophore groups (24). These interactions which are also responsible for excitation delocalization cause wavelength shifts (bathochromism and hypsochromism) such as in dye aggregates and molecular crystals (25, 26), and intensity changes (hypochromism or hyperchromism) in these species, in double chain polynucleotides

(27) and in helical polypeptides (28). An excellent review concerning the subject of weakly interacting chromophores and the resulting spectral changes is given by Murrell (24).

The absorption spectra of LI and LII (Figure III) do not differ very much from that of an equimolar mixture of 4-methylbenzophenone ($\epsilon \cong$ 70 at 3130 Å ) and 1-methylnaphthalene ($\epsilon \cong$ 300 at 3130 Å). The difference spectra for LI and LIII are similar and could result from a bathochromic shift of an upper naphthalene or benzophenone transition in LI and LIII, or could result from a new transition arising from an interaction between higher excited states of LI and LIII . At any rate, the difference spectra are not very "intense" at 3130 Å and so it is safe to assume that use of excitation of 3130 Å wavelength leads predominantly to excitation of the naphthalene chromophores in LI and LIII to their lowest excited singlet states.

The absorption spectrum of LII shows a significant hyperchromicity relative to that of an equimolar mixture of 4-methylbenzophenone and 1-methylnaphthalene (Figure III). As can be seen in the difference spectrum, both the $n \rightarrow \pi^*$ transition in the benzophenone chromophore and the lowest transition in the naphthalene chromophore show an intensity increase of about 50%. Here too it is safe to say that most of the exciting light of 3130 Å wavelength absorbed is absorbed by the naphthalene chromophore.

The interactions leading to the differences in the absorption spectra of the Leermakers' Compounds are no doubt extremely geometry dependent. A discussion of the specific interactions is beyond the scope of this thesis. Furthermore, important information concerning the geometries of the Leermakers' Compounds would be difficult to obtain. Some observations concerning the geometries are discussed below.

Extending the saturated carbon bridge from one to three methylene groups does not significantly alter the "distance" between the chromophores in the Leermakers' Compounds. In an attempt to obtain information about the geometries, molecular models (Leybold) were constructed. However, no conformations significantly different from those possessed by the models of LI and LIII were unique in the model of LII. It is not at all obvious from the molecular models why the absorption spectrum of LII differs significantly from the spectra of LI and LIII. The models show only that LIII can "explore" more intermediate conformations than can LII, and in turn LII can "explore" more than LI. What the preferred conformations are in each case is not obvious either. The effect of temperature and solvent upon relative conformer populations may be significant.

Some information concerning the directions of polarization of the two lowest ground to excited singlet transition is available for naphthalene and benzophenone (29, 30, 31), but this information is useless without information concerning the geometries of the Leermakers' Compounds.

## Triplet Excitation Transfer

The fact that no emission characteristic of benzophenone is observed from the Leermakers' Compounds, even when the exciting light is absorbed by the benzophenone moiety, and intense (compared to that from 1-methylnaphthalene) naphthalene-like phosphorescence is observed, is most easily explained by postulating that efficient transfer of triplet excitation from the benzophenone moiety to the naphthalene chromophore occurs. However, these data offer no proof that the excitation was transferred *via* the benzophenone moiety triplet rather than directly from the benzophenone singlet (the transfer involving a multiplicity change). But the results of the chemical quenching experiments ("chemical spectroscopy") do offer additional information in this regard. The experiments involving photostationary states of the piperylene system (Table IV) clearly show, as did the phosphorescence spectra, that although only the benzophenone groups absorned the exciting light, efficient energy transfer occurs, resulting in formation of the naphthalene moiety triplets. However, a close look at the data reveals that at the high quencher concentration used, there may be some interception of benzophenone moiety triplets. This results in $(\underline{t}/\underline{c})_{p.s.s.}$ values lower than that expected if only naphthalene group triplets were quenched (2.16-2.18). The $(\underline{t}/\underline{c})_{p.s.s.}$ values using the Leermakers' Compounds as sensitizers with 0.2 M piperylene range from 2.03 to 1.97, which can be explained if 10-12% quenching of benzophenone moiety triplets occurs (see Table IV). As expected, lowering the quencher concentration (0.05 M) results in less efficient interception of benzophenone chromophore triplets and higher $(\underline{t}/\underline{c})_{p.s.s.}$ values, 2.07-2.11. These results clearly demonstrate the intermediacy of the benzophenone group triplet in the energy transfer scheme.

The triplet yield data for 3660 Å excitation (Table V) show that energy quantum absorbed by the benzophenone chromophore in the Leermakers' Compounds results in the formation of a quenchable triplet. Combining these results with the results from the photostationary state measurements for 0.05 M piperylene leads to the following conclusion. Irradiation of the Leermakers' Compounds (n = 1, 2, 3) with light of 3660 Å wavelength leads to excitation of the benzophenone chromophore to its lowest $n \rightarrow \pi^*$ singlet state. After completely efficient intersystem crossing resulting in the corresponding $n \rightarrow \pi^*$ triplet, transfer of the triplet excitation to the naphthalene group takes place with 100% efficiency. This path for the excitation energy is shown in Figure II.

The phosphorescent lifetime of benzophenone is $5 \cdot 10^{-3}$ sec (32), and this is close to the true radiative lifetime (7). Since no emission characteristic of benzophenone is observed from the Leermakers' Compounds, triplet excitation transfer must occur at the rate of at least $1000 \times 1/\tau_p = 2 \cdot 10^5$ sec$^{-1}$. However, the data from the chemical quenching experiments demand a much faster transfer rate. Transfer of triplet excitation from benzophenone to both cis- and trans-piperylene occurs at the diffusion-controlled rate (7). If the quenching of the benzophenone moiety triplets in the Leermakers' Compounds follows the rate law: quenching rate = $k_q$ [piperylene][triplet], where $k_q$ is the diffusion-controlled bimolecular rate constant, then the intramolecular triplet transfer rate can be determined from the photostationary state data. The fractions of benzophenone chromophore triplets that must be intercepted in order to account for the observed photostationary states are listed in Table VI. In the presence of 0.2 M piperylene, the rate of intramolecular triplet transfer is about a factor of ten greater than the rate of piperylene quenching of benzophenone moiety triplets in all three Leermakers' Compounds. In the presence of 0.05 M piperylene, intramolecular transfer is twenty to thirty times faster than piperylene quenching of benzophenone group triplets. Since $k_2$, the bimolecular quenching constant, is about $10^{10}$ liter mole$^{-1}$ sec$^{-1}$,

# TABLE VI

Interception of Benzophenone Chromophore Triplets

(Benzene solution; room temperature; 3660 Å excitation)

| Sensitizer | Conc. Piperylene | $(\underline{t}/\underline{c})_{p.s.s.}$ | % Benzophenone moiety triplets quenched |
|---|---|---|---|
| 4-Methylbenzophenone | --- | 1.25 | [ 100] |
| 1-Methylnaphthalene | --- | 2.16 | [ 0] |
| LI | 0.20 | 2.03 | 9 |
| | 0.05 | 2.10 | 3 |
| LII | 0.20 | 1.99 | 11 |
| | 0.05 | 2.11 | 3 |
| LIII | 0.20 | 1.97 | 13 |
| | 0.05 | 2.07 | 5 |

Calculation of these values is based on the mechanism for the photosensitized isomerization as given by Hammond *et al*. (7). For a single sensitizer, the piperylene photostationary state isomer ratio is independent of piperylene concentration.

the intramolecular triplet transfer rate must be about $1\text{-}2\cdot 10^{10}$ $\sec^{-1}$. However, the calculated fractions of benzophenone chromophore triplets quenched are very close to the fractions of benzophenone moieties expected to have at least one piperylene molecule as a nearest neighbor, about 8% at 0.2 M piperylene and about 3% at 0.05 M piperylene (33). One might conclude, then, that the transfer rate is much greater than $10^{10}$ $\sec^{-1}$, and so only those piperylene molecules which are nearest neighbors to the benzophenone moiety at the time it is in its triplet state are effective in quenching. This picture demands that nearest neighbor intermolecular transfer (quenching by piperylene) be more efficient than the intramolecular transfer. Thus, the chemical quenching experiments allow only a lower limit determination of the intramolecular triplet transfer rate. The rate of intramolecular triplet excitation transfer from the benzophenone chromophore to the naphthalene chromophore in the Leermakers' Compounds is at least $10^{10}$ $\sec^{-1}$.

Some comments concerning the mode of triplet excitation transfer in the Leermakers' Compounds conclude this section. Triplet excitation transfer in the Leermakers' Compounds might occur by an exchange interaction involving overlap of chromophore electron clouds, by exciton migration not involving overlap or because of interactions involving the methylene bridge. From an older model of Perrin, Terinen and Ermolaev (5) defined a "sphere of quenching action" for intermolecular triplet excitation involving an exchange mechanism. If the excited molecule has a quenching agent within a "sphere of quenching action," the excited molecule is "instantaneously deactivated without emitting." On the other hand, a quencher located outside the sphere exerts no effect upon the excited molecule. There seems to be good evidence for this "sharp cut-off" model for triplet excitation transfer (34, 35). The radius of the "sphere of quenching action" for the benzophenone-naphthalene system was found to be about 13 Å. Measurements on the molecular models of the Leermakers' Compounds show, as expected, that the distance between the carbonyl carbon atom and the center of the naphthalene moiety is at most about 10 Å in all three cases. El-Sayed (36) claims that there is a preferred geometry for most efficient triplet excitation transfer from benzophenone to phenanthrene which has the plane of the phenanthrene molecule parallel to the carbonyl carbon-oxygen bond axis. All three Leermakers' Compounds can assume reasonable conformations which fulfill the El-Sayed favored geometry.

Using Förster's model, it can be calculated (equation 4) that the distance required between the centers of a benzophenone molecule and a naphthalene molecule to effect 50% triplet exciton transfer <u>via</u> a dipole-dipole interaction is 1 Å (4). However, the approximations contained in the Förster model break down at much larger distances. Furthermore, at the close approach of chromophores, as found in the Leermakers' Compounds, higher multipole interactions (electric dipole-quadrupole, electric dipole-magnetic dipole, etc.) could contribute significantly to exciton migration.

The matrix element for transfer of an electron or electronic excitation between two identical chromophores connected by a "bridge" of identical groups (e.g. methylene groups) or between two identical guest molecules separated by a linear chain of host molecules is given by equation 9 (37, 38, 39),

$$\beta_N = (f_\beta \beta_o)^2 (f_{\beta'} \beta_o')^{N-1} (-\Delta E)^{-N} \qquad N \geq 1 \qquad (9)$$

where N is the number of units in the "bridge" or the number of hosts in between the two guests; $\Delta E$ is the zero-order energy difference between the excitation energy of the free chromophore or guest, and that of the free "bridge" unit or host; $\beta_o$ represents the purely electronic interaction between the chromophore and "bridge" unit, or between the guest and host; and $\beta_o'$ is the "bridge" unit-"bridge" unit or host-host nearest neighbor electronic interaction matrix element. The quantities $f_\beta$ and $f_\beta'$ are vibrational factors equal to the square of vibrational overlap integrals between appropriate pairs of states. Equation 9 is a perturbation result good only in the limit $\Delta E >> f_\beta \beta_o, f_\beta' \beta_o'$. A rough estimate of the transfer rate $k_N$ can be obtained from the uncertainty principle, and is given by equation 10. The application of equation 9 to triplet transfer <u>via</u>

$$k_N = \frac{1}{\tau_N} = 4\, h^{-1}\, \beta_N \qquad (10)$$

the methylene bridges in the Leermakers' Compounds is not straightforward for a number of reasons. The chromophores are not identical, and so two different chromophore-methylene group matrix elements, $\beta_o(1)$ and $\beta_o(2)$, and two different "bridge"-chromophore energy gaps, $\Delta E(1)$ and $\Delta E(2)$, should be incorporated. However, for a rough estimate, $\beta_o(1)$ and $\beta_o(2)$ can be taken to be equal, about 300 cm$^{-1}$, and $\Delta E(1)$ and $\Delta E(2)$ can be taken to be equal, about 20,000 cm$^{-1}$. The methylene group-methylene group electronic interaction matrix element $\beta_o'$ is not known, but a reasonable value would be 1000 cm$^{-1}$. Another serious limitation concerns the "locale" of the triplet excitation in the benzophenone moiety. If the triplet excitation is "localized" in the carbonyl group, then two "bridges" must be considered, the methylene "bridge," and the benzene ring that separates the carbonyl group and the methylene bridge. Furthermore, the strong interaction and small energy gap between carbonyl (formaldehyde-like) triplet and the benzene triplet precludes a perturbation treatment. For the purpose of discussion, the possible "localization" of the triplet excitation to the carbonyl group will be ignored and the rate of transfer of triplet excitation will be calculated from equation by considering only the methylene "bridge." For $k_N = 10^{10}$ sec$^{-1}$, a $\beta_N$ value of about 0.1 cm$^{-1}$ is necessary (equation 10). For $\Delta E = 20,000$ cm$^{-1}$, $\beta_o = 300$ cm$^{-1}$, $\beta_o' = 1000$ cm$^{-1}$ and $f_\beta = f_\beta' = 0.1$, $\beta_N$ is .05 for N = 1, $10^{-4}$ for N = 2, and $10^{-6}$ for N = 3. Even if $f_\beta = f_\beta' = 1$, $\beta_N$ is 5 for N = 1, 0.2 for N = 2, and $10^{-2}$ for N = 3. Two interesting points can be made based upon these calculations. The first is that for the reasonable parameter values chosen, equation 9 does not predict the triplet transfer rate observed for LIII, $10^{10}$ sec$^{-1}$. However, it must be kept in mind that equations 9 and 10 are only approximations. More important is the second point. Equation 9 predicts a large fall-off in the transfer rate with an increase in the number of "bridge" units if $\Delta E$ is large, and $f_\beta \beta_o'$ is small. The drop-off factor for an increase in "bridge" length by one unit is $\Delta E/f_\beta'\beta_o'$. For $\Delta E = 20,000$ cm$^{-1}$, $f_\beta' = 1$ and $\beta_o' = 1000$ cm$^{-1}$, increasing the "bridge" length by one unit reduces the rate of transfer by a factor of 20.

Two observations which may be extracted from the chemical quenching experiments (vide supra) are that the rate of triplet excitation transfer in the Leermakers' Compounds is > $10^{10}$ sec$^{-1}$, and that the transfer rate must be nearly the same for all three cases. Thus, it is not likely that the methylene "bridges" are involved to any significant extent in the transfer of triplet excitation in the Leermakers' Compounds since an expected large dependence of the transfer rate on the "bridge" length is not observed. Whether the lack of a geometry effect on the transfer rate is more consistent with an exchange mechanism or an exciton mechanism is not clear. Certainly one might expect a geometry effect on the rate of transfer via an exciton mechanism. However, if higher multipole-multipole interactions than the dipole-dipole interaction contribute significantly, the effect of changes in the relative orientation of the two chromophores would be diminished. Furthermore, one can also envision geometry effects on the exchange interactions due to overlap of electron clouds. This is reflected in El-Sayed's observation (36) of a favored geometry for triplet excitation transfer from benzophenone to phenanthrene. Intermolecular transfer of triplet excitation in fluid solution by the exchange mechanism can occur at the diffusion-controlled rate, that is, at every collisional encounter. Encounter times in typical organic solvents at room temperature are on the order of $10^{-11}$ sec (40). Thus, the exchange mechanism can account for the observed rate of triplet excitation transfer in the Leermakers' Compounds. No estimate of the rate of transfer by an exciton mechanism can be made.

Finally, theoretical calculations (41) predict that the excitation energy of second triplet state of naphthalene is very close to that of the first excited benzophenone singlet. Thus, triplet transfer from benzophenone to napthalene must only involve the lowest naphthalene triplet state.

## Singlet Excitation Transfer

The fluorescent emissions from the Leermakers' Compounds (Figures VII, IX, and X) using 3130 Å exciting light are much less intense than that observed from 1-methylnaphthalene (Figure VI) under the same conditions. On the basis of the absorption spectra of the Leermakers' Compounds, one can conclude that most of the light of 3130 Å wavelength is absorbed by the naphthalene moities. The fractions absorbed by the naphthalene groups in LI and LII cannot be determined exactly without knowing the nature of the difference spectra (vide supra). However, in the case of LII where a hyperchromic effect leads to an approximately equal intensification of both the benzophenone group $n \rightarrow \pi^*$ transition and the naphthalene long-wavelength transition, about a 20:80 partition of 3130 Å exciting light between the benzophenone and naphthalene groups, respectively, operates. Thus, the intensities of the fluorescent emissions from the Leermakers' Compounds are much lower than expected on the basis of their absorption spectra and on the basis of the fluorescent intensity of 1-methylnaphthalene (Figure VI). That this decrease in fluorescent intensities in the Leermakers' Compounds can be attributed to intramolecular singlet excitation transfer from the naphthalene moities to the benzophenone chromophores is evidence by the concomitant increase in the phosphorescent intensities. In the previous section it was shown that excitation of the benzophenone groups leads to totally efficient formation of the naphthalene chromophore triplet. Thus, singlet excitation transfer from the naphthalene chromophores to the benzophenone groups should lead to an increase in the intensity of the naphthalene moiety phosphorescence. From the total emission spectra it can be seen, at least qualitatively, that the decrease in fluorescence intensities is compensated by an increase in phosphorescence intensity.* The quantitative data in the efficiency of naphthalene moiety triplet formation in the Leermakers' Compounds upon excitation with 3130 Å light (Table V ) strongly indicates the singlet excitation transfer operates. Assuming 70-80% of the light is absorbed by the naphthalene moiety and a 0.5 intersystem crossing efficiency, 35-40% of the quanta absorbed lead to naphthalene group triplets. Add the 20-30% formed via triplet excitation transfer from the benzophenone moieties directly excited, and the total efficiency of naphthalene moiety triplets is expected to be 0.55-0.70. But the triplet "counting" data indicate 0.98 for LI, 0.80 for LII, and 0.94 for

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* It must be kept in mind that only about 10% of the naphthalene triplets undergo radiative decay while non-radiative $S_1 \rightarrow S_0$ decay in naphthalene is probably not very important (7).

LIII.* Thus, unless the presence of the benzophenone groups leads to very efficient intersystem crossing in the naphthalene chromophores, the high yield of naphthalene group triplets under 3130 Å excitation can only be accounted for if singlet excitation transfer occurs from the naphthalene group to the benzophenone group where totally efficient intersystem crossing operates. The fact that the carbonyl function is necessary for the decrease in fluorescent intensities and increase in the phosphorescent intensities in the Leermakers' Compounds is indicated by the total emission spectrum (Figure VIII) and triplet yield (Table V) of the LI-alchol which are not very different from those exhibited by 1-methylnaphthalene.

The most convincing evidence for the involvement of the first excited singlet state of the benzophenone moiety in the triplet yield enhancement scheme may be drawn from the shapes of the fluorescence spectra of the Leermakers' Compounds. Compared to the fluorescence spectrum of 1-methylnaphthalene, the fluorescence spectra of the Leermakers' Compounds show diminished intensity

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* At the concentrations used in the triplet "counting" experiments (0.01 M), intermolecular transfer of singlet excitation by the "trivial" process should be important. However, the low concentration (0.001 M) fluorescence spectra of the Leermakers' Compounds (Figures VII, IX, X ) exhibit little intensity in the region where the benzophenone groups absorb. Thus, the measured triplet yields are close to the values expected if no intermolecular singlet excitation were occurring.

chiefly in the region of the $n \rightarrow \pi^*$ absorption band of the benzophenone groups. This observation is most easily realized in the case of LII.

Thus, one may follow in detail the paths of excitation transfer in the Leermakers' Compounds (Figure II). In the Leermakers' Compounds, intramolecular singlet excitation transfer from the lowest excited singlet state of the naphthalene groups to the lowest $n \rightarrow \pi^*$ singlet state of the benzophenone chromophores occurs with high but not with total efficiency. Totally efficient intersystem crossing operates in the benzophenone moieties and the triplet excitation is transferred to the naphthalene groups with 100% efficiency. Since the intersystem crossing efficiency in the naphthalene groups is only about half that for benzophenone, the overall effect of the transfers is an enhancement of the yield of naphthalene group triplets.

A calculation using the Förster relationship (equation 7) reveals that singlet excitation transfer from 1-methylnaphthalene to 4-methylbenzophenone by a dipole-dipole exciton mechanism would achieve 50% efficiency at a distance of about 50 Å between the two molecules. Thus, one might expect that totally efficient intramolecular transfer by the exciton mechanism would operate in the Leermakers' Compounds because of the large inverse distance dependence. Furthermore, at such close approach of the chromophores, higher multipole interactions could also contribute. Interactions between the chromophores via the methylene "bridge," as discussed in the last section, might also be expected to be large enough to affect singlet excitation transfer. Finally, exchange interactions due to overlap of electronic clouds, which might be the favored route for triplet excitation transfer, could also operate in the case of singlet excitation transfer. Transfer by any of these mechanisms should not affect the shape of the donor emission spectrum. As has already been mentioned, the shape of the fluorescence spectra of the Leermakers' Compounds can be accounted for by assuming that a transfer mechanism having the spectral characteristics of the "trivial" emission-reabsorption mechanism operates. The fluorescence spectrum of LII can be fairly closely matched by "subtracting" the long-wavelength absorption band of benzophenone from the fluorescence spectrum of 1-methylnaphthalene. This is not the case for LI and LIII. The fluorescence spectra of the latter also show diminished intensity in the wavelength region (>3900 Å) where benzophenone does not absorb. Thus, there are at least two singlet excitation transfer mechanisms operating, one which does not change the shape of the donor emission and one which has at least that characteristic of the "trivial" process, namely distortion of the donor emission spectrum. In the case of LII, the latter mechanism dominates, whereas for LI and LIII, the former mechanism contributes significantly. It is mentioned again that at least at the sampe size and concentrations employed ($10^{-3}$ M), little, if any, intermolecular transfer takes place. At any rate, the fluorescence spectrum of 1-methylnaphthalene is hardly affected by the presence of benzophenone ($10^{-3}$ M) in the solution (Figure Finally, not only is singlet excitation transfer less efficient (about 75% in LII, 85% in LIII, and 90% in LI) than triplet transfer (100% in all cases), but the rate of singlet energy transfer ($k \sim 10^{7} - 10^{8}$ $sec^{-1}$) is much slower than the rate of triplet excitation transfer ($k > 10^{10}$ $sec^{-1}$) in the Leermakers' Compounds.

As mentioned previously, Schnepp and Levy ( 21) concluded that the extent of singlet transfer in the naphthalene-anthracene compounds III, IV, V, is nearly the same 0.3 ± 0.13 in all compounds. Thus, even in this case the rate of intramolecular singlet excitation transfer is about $10^{7}$ $sec^{-1}$. Schnepp and Levy stated ( 21 ) that the measured efficiencies ($\sim$.3) mean that the transfer competes successfully with naphthalene group fluorescence but cannot compete with the radiationless processes that normally occur from the naphthalene moiety singlets. This interpretation cannot be correct since the rate of fluorescence and the rate of radiationless decay (intersystem crossing, etc.) from the first excited singlet state of naphthalene (or 1-methylnaphthalene) are nearly the same (7). Thus, if only 30% or so of the naphthalene group singlets transfer energy to the anthracene chromophores, and the remaining 60% partition between radiative and other radiationless decay paths in a rate not very different from the ratio in naphthalene (or 1-methylnaphthalene), then some residual naphthalene group fluorescence should have been observed by Schnepp and Levy. They reported that no emission which could be assigned as naphthalene-like fluorescence was detected, and only anthracene group fluorescence was observed. However, if distortion of the donor emission spectrum such as is observed for the Leermakers' Compounds also occurs in the naphthalene-anthracene compounds, most of the "residual" naphthalene group fluorescence might be "buried" under the intense anthracene moiety fluorescence. A careful study of the spectra of these interesting compounds should be carried out.

Distortion of donor emission characteristic of the "trivial" process has also been observed in biphenyl crystals "doped" with anthracene. Bhaumik ( 42, 43) has shown that the usual broad band fluorescence spectrum of biphenyl crystals assumes a structured appearance when the crystal is "doped" with a small amount of anthracene. The structure can be accounted for exactly if absorption of biphenyl emission by anthracene is assumed. However, Bhaumik showed unequivocally that at the anthracene concentrations employed, the ordinary picture envisioned for the "trivial" process cannot possibly account for the observations. For instance, in one set of experiments, the emission from a biphenyl crystal was examined after being "filtered" through one of the biphenyl crystals "doped" with anthracene. There was no change in the biphenyl emission spectrum. It has been claimed (44) that the fluorescent emission from anthracene crystals crystals comes from anthracene molecules next to lattice defects or impurity sights, and that the anthracene fluorescence from anthracene crystals "doped" with naphthacene comes chiefly from anthracene molecules. Thus, if in the anthracene-"doped" biphenyl crystals the biphenyl fluorescence comes chiefly from biphenyl molecules which are nearest neighbors to anthracene molecules, the situation and results are similar to those for the Leermakers' Compounds, especially LII. That is to say, the acceptor enhances the rate of fluorescence in the donor (the large hyperchromic effect in LII) and the nature of the excitation transfer mechanism is such that the donor emission spectrum is distorted in a way expected if the "trivial" emission-reabsorption mechanism were operating. That emission and reabsorption is actually occurring over such a short range is doubtful. However, no other easy explanation of the observations is available.

As mentioned, the directions of polarization of the $S_0 \rightarrow S_1$ transitions in naphthalene and benzophenone have been determined. With this information in hand, it would be very interesting and most informative to examine compounds containing the two chromophores in known fixed relative orientations. The syntheses of such compounds, although not simple undertakings, should be possible. Determination of the naphthalene group fluorescent lifetimes would also yield useful information. Certainly with the techniques described in this thesis, detailed information concerning intramolecular transfer in many interesting model compounds can be easily obtained.

# EXPERIMENTAL

## Materials

### The Leermakers' Compounds

The Leermakers' Compounds were supplied by Dr. P. A. Leermakers. They were synthesized by Mr. G. Byers using straightforward conventional organic synthetic methods. A full report on the syntheses, purification, and physical data for the compounds can be found in his thesis (45).

### LI-alcohol

LI-alcohol was obtained by reducing the carbonyl group of LI using excess lithium aluminum hydride in ether. The details of the syntheses, purification, and physical data for the compound can be found in Mr. Byers' thesis (45).

### 1-Methylnaphthalene

See the experimental section of Part I.

### Benzophenone

See the experimental section of Part I.

### 4-Methylbenzophenone

See the experimental section of Part I.

## EPA

EPA is a mixture of ether, isopentane, and ethyl alcohol in the ratio 5:5:2 by volume. The isopentane was Phillips Pure Grade which was passed through alumina and distilled prior to use. Only freshly opened absolute ether was used. The ethyl alcohol was absolute and was distilled prior to use.

## Emission Spectra

A photoelectric spectrophosphorimeter consisting of a Jarell-Ash Ebert scanning grating monochrometer (f/9), an EMI 9558 photomultiplier tube, a "rotating" can phosphoroscope, an electrometer amplifier, and a strip chart recorder, was used to record the emission spectra. The degassed samples were contained in sealed pyrex tubes (10 mm I.D.) held in a pyrex dewar containing liquid nitrogen. A G.E. AH-4 mercury lamp was the excitation source. A combination of Corning CS-7-37 and CS-0-52 glass filters was employed to isolate the group of lines near 3660 Å. A narrow band interference filter was used to isolate the group of lines near 3130 Å. The emissions were viewed at right angles to the direction of the exciting light. For total emission spectra, the phosphoroscope was removed. All spectra were recorded at a scanning rate of 50 Å/min. A correlation of scanning rate and recorder chart speed allowed wavelength determination (±5 Å) directly from the recorded spectra. The wavelength indicator on the monochrometer was calibrated from time to time using the mercury lines as standards. None of the spectra were corrected for the spectral sensitivity of the apparatus.

The samples were carefully made solutions in EPA. All the concentrations reported in this thesis are room-temperature concentrations. The concentrations at 77° K are a little higher, since the EPA contracts to about 2/3 the room-temperature volume when frozen at 77° K.

## Phosphorescent Lifetimes

Phosphorescent lifetimes were determined with the use of two manually operated shutters, the first between the excitation source (G.E. AH-4 mercury lamp plus appropriate filters) and the sample (an EPA solution contained in a sealed pyrex tube within a pyrex dewar filled with liquid nitrogen), and the second between the sample and a photomultiplier tube (R.C.A. 1-P28). The signal from the photomultiplier tube was amplified and displayed on an oscilloscope equipped with a Polaroid camera. The initial conditions were with the second shutter in place and the first shutter displaced so that exciting light impinged upon the sample but no emitted light reached the photomultiplier tube. Then simultaneously, the first shutter was put in place, the second shutter displaced, the sweep on the oscilloscope triggered, and the camera shutter opened. After the decay curve was photographed, the camera shutter was closed. The unimolecular decay rates were determined from the decay (intensity *vs.* time) curves, which were all exponential. The values for naphthalene and 1-methylnaphthalene agreed well with the several values reported in the literature. The literature values ranged from 2.1 to 2.3 sec, while 2.3 sec was obtained in this determination.

### Piperylene Photostationary States

Carefully prepared samples containing sensitizer (LI, LII, or LIII) and either *cis*- or *trans*-piperylene (see Part I) in Phillips Research Grade benzene were loaded into 13 x 100 mm pyrex test tubes. The samples were degassed by the freeze-pump-thaw method (see Part I) and sealed under vacuum. Irradiation with light of 3660 Å wavelength employing the "merry-go-round" (see Part I) equipped with Corning glass filters CS-7-37 and CS-0-52 for twelve hours was sufficient to achieve photostationary isomer mixtures. The photostationary isomer ratio was determined by vapor phase chromatography (see Part I).

## Triplet Yields

A detailed description of the "triplet counting" method employed is given in Part I of this thesis. Triplet yields for all the compounds mentioned in Part II were determined using *cis*-piperylene as the quencher.

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# PROPOSITION I

Two mechanisms are proposed for the copper chloride catalyzed reaction of 1, 3, 3-trimethylcyclopropene to give 1, 1, 2, 5, 6, 6-hexamethylhexatriene. An experiment is proposed to differentiate between them. Synthetic applications are discussed

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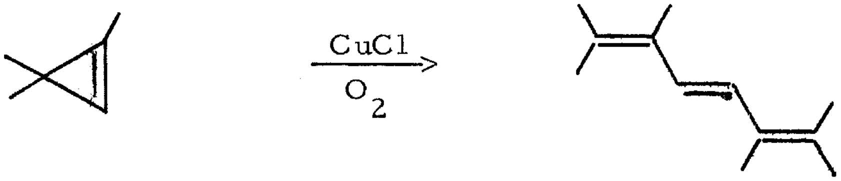
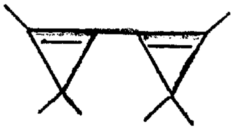
Stechl (1) reported that treatment of 1, 3, 3-trimethylcyclopropene (I) with copper chloride and oxygen did not give the expected oxidative coupling product III but gave 1, 1, 2, 5, 6, 6-hexamethylhexatriene (II) in good yield.* It is proposed that the transformation does not require oxygen, and that one of the following mechanisms operates.



I

II



III

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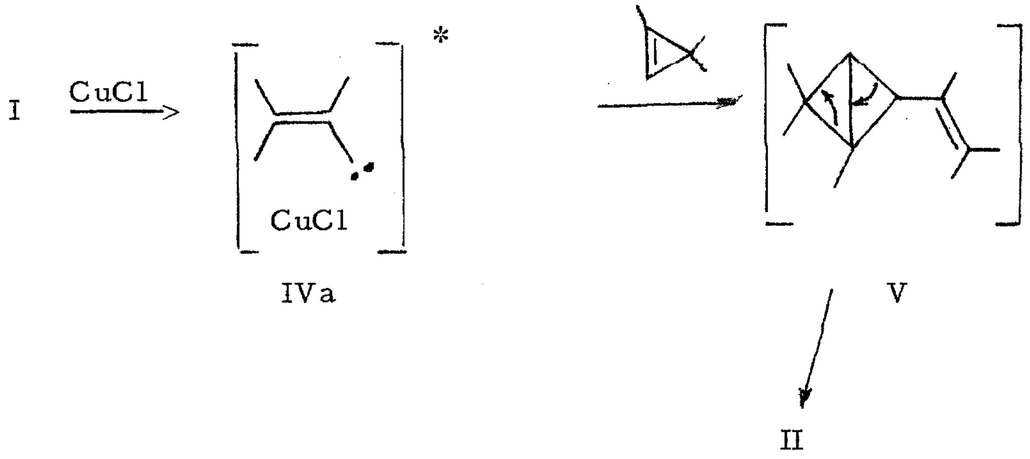
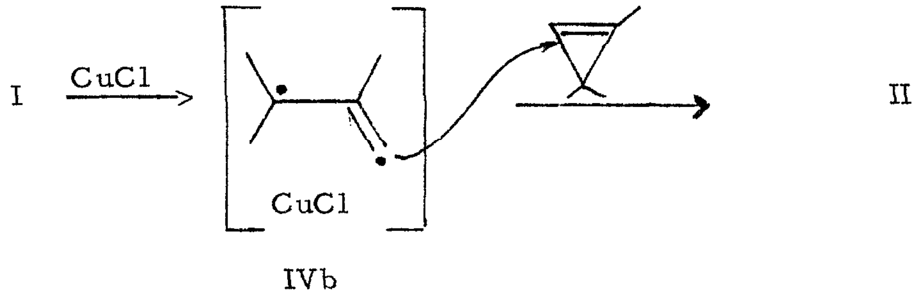
[*] The yield and whether only one hexatriene isomer is obtained was not reported.

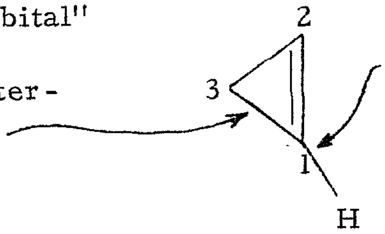
Mechanism I (complexed-carbene intermediate)



Mechanism II (complexed-biradical intermediate)



1-carbon "orbital" has much 'p'-character-weak bond



carbon "orbital" has 44% 's'-character

VI

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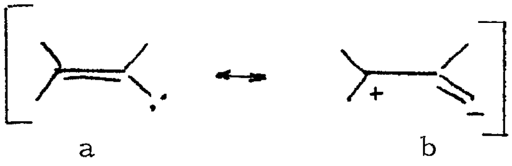
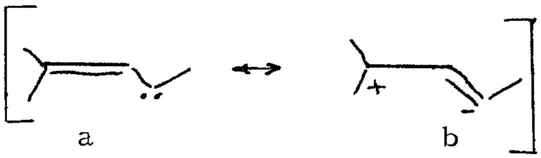
[*] The structure of the complex and whether CuCl or CuCl$_2$ is involved cannot be specified. There are several examples (2,3,4) of carbene-copper salt complex formations reported in the literature. No detailed structures have been suggested for any of them and no structure determinations have been undertaken.

Closs (5) has shown ($^{13}$C-H nuclear spin-spin coupling constant determination) that the carbon atomic orbital used for bonding of hydrogen in the vinyl hydrogen bonds of cyclopropene (see Structure VI) exhibits 44% of 's'-character. The acidity of the vinyl proton also indicates that cyclopropenes appear to be more closely related to acetylenes than to olefins. The $C_1$-carbon atomic orbital used for bonding of the $C_3$-carbon atom must, then, have much 'p'-character and the $C_1$-$C_3$ bond is a "weak" bond (a "bent" bond) (5, 6). In the case of the reaction of I, the ring could open two ways. Although it is possible that more than one isomer was produced, only one hexatriene was isolated. But the direction the ring would have to open to give the observed product would be, in fact, the favored direction. This is most easily seen by considering the dipolar structures for the ring-opened species, IVb and VIIIb. The electron-releasing effect of the methyl group should destabilize VIII relative to IV.



IV



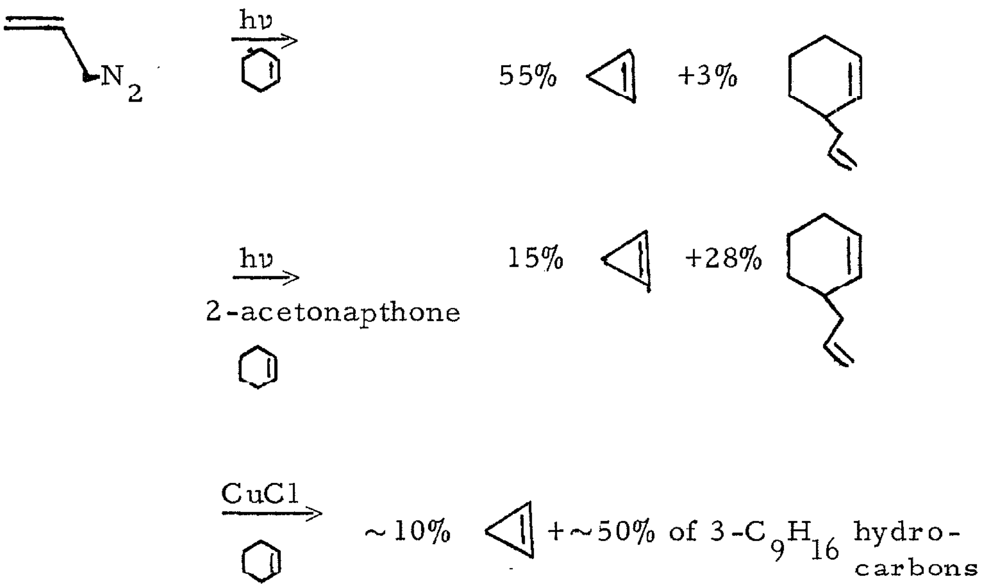
VIII

Both mechanisms involve ring opening of the same bond, but differently reacting intermediates are produced. In mechanism I, the intermediate has a complexed-carbene nature and addition to the double bond of the second cyclopropene molecule is proposed as its reaction mode. The role of copper or its salts in modifying the reactivity of carbenes when generated from diazo compounds is well known (3,4,5) and probably involves a complex of the carbene with the copper surface or with a copper salt. It is the consensus that these complexed carbenes do not react as "free" carbenes (5,7) in additions to double bonds. Rather, the methylene-moiety is transferred from the complex to the olefin. The bicyclobutane produced opens to give the hexatriene.

Mechanism II involves a species with radical character. A radical "displacement" at a weak bond in a second cyclopropene molecule gives the hexatriene directly.

Both mechanisms predict two hexatriene products. There are two ways to open the bicyclobutane and two positions for radical attack. Since only one hexatriene was isolated, it is likely that it is produced in much larger yield than the other possible products. Although it is difficult to explain why the proposed bicyclobutane intermediate would open one way in particular, steric effects could direct the radical attack to the carbon atom which does not possess the methyl group.

Finally, whereas the photolytic decomposition of diazopropene using cyclohexene as solvent gives cyclopropene and a small amount of 3-allylcyclohexene (IX), the photosensitized decomposition of diazopropene in cyclohexene gives cyclopropene and a larger amount of 3-allylcyclohexene. On the other hand, the CuCl-catalyzed decomposition in cyclohexene gives much less cyclopropene and a good yield of a mixture of $C_9H_{16}$ hydrocarbons (8). Unfortunately, the structures of the latter have not yet been determined (none is either 3-allylcyclohexene or 2-allylcyclohexene). The direct and sensitized (9) decomposition give the "free" singlet and triplet carbene, respectively. The fact that the CuCl-catalyzed decomposition evidently yields significantly different products (perhaps addition products involving the cyclohexene double bond), can be interpreted in terms of a copper salt-complexed intermediate.[*]



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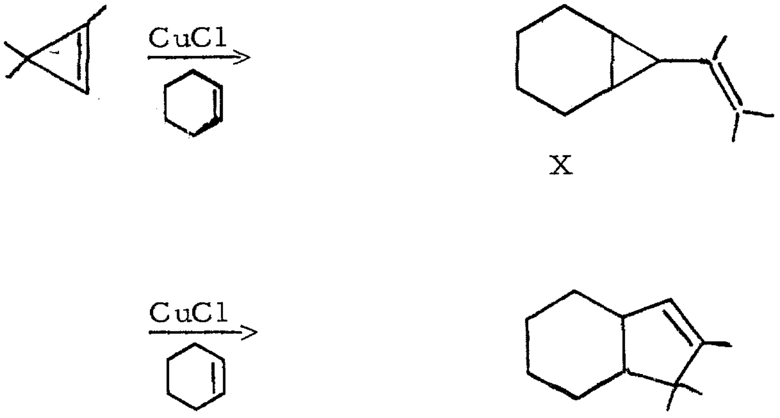
[*] The CuCl-catalyzed decomposition could give only cyclopropene followed by CuCl-catalyzed reaction of cyclopropene and cyclohexene.

The CuCl-catalyzed reaction of I in cyclohexene would present clear evidence for or against the mechanisms proposed. If only

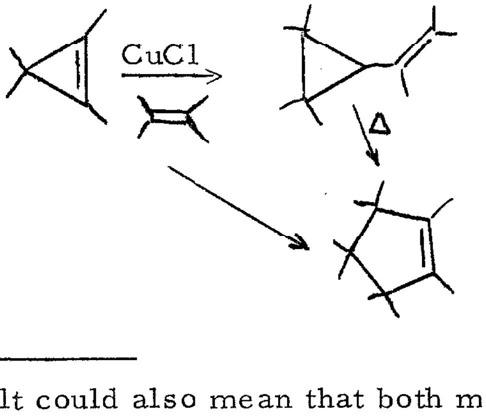


X

XI

the cyclopropane product X is obtained, then mechanism I is favored. If, in addition, the cyclopentene XI is obtained, mechanism II is favored.*

If the reaction with cyclohexene proceeds in good yield, its application in the synthesis of 5-membered carbocyclic rings is straightforward.



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* This result could also mean that both mechanisms operated.

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# PROPOSITION II

It is proposed that tetrazomethane can be prepared and isolated and that the compound would be an excellent source of atomic carbon in both the gaseous and the condensed phase.

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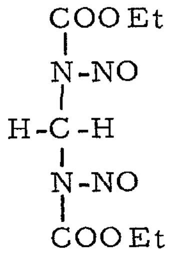
In 1929, Holter and Bretschneider (1) reported their attempts to prepare tetrazomethane (I). The method they chose was to treat

$$\underline{\bar{N}}-\bar{N}=C=\bar{N}-\underline{\bar{N}}$$

I (one resonance form)

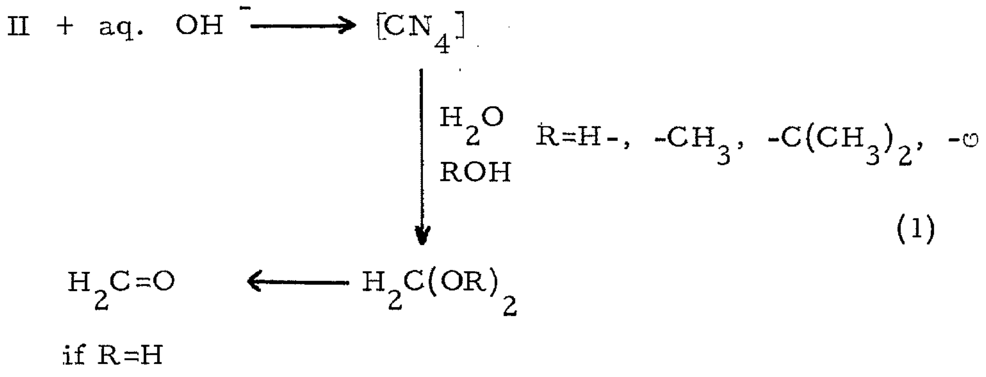
the bis-nitrosourethan compound II with aqueous hydroxide ion in a



$$\begin{array}{c} COOEt \\ | \\ N-NO \\ | \\ H-C-H \\ | \\ N-NO \\ | \\ COOEt \end{array}$$

II

variety of hydroxlyic solvents. Although they did not isolate $CN_4$, the investigators reported good evidence for its existence as a fast reacting intermediate under their reaction conditions. For instance, they obtained good yields of formaldehyde when the reaction was carried out in water, and good yields of the appropriate bis-alkoxymethylene when the reaction was carried out in an alcohol solvent.



$$\begin{tikzcd}[column sep=large]
 & \text{II} + \text{aq. } OH^- \arrow[r] & {[CN_4]} \arrow[d, "\begin{array}{l} H_2O \\ ROH \end{array}"] & R{=}H\text{-},\ \text{-}CH_3,\ \text{-}C(CH_3)_2,\ \text{-}\phi \\
 & \begin{array}{c} H_2C{=}O \\ \text{if } R{=}H \end{array} & H_2C(OR)_2 \arrow[l] &
\end{tikzcd}$$

(1)

It is proposed that the general approach of Holter and Bretschneider is satisfactory and that with certain modifications of their procedure, such as the use of aprotic polar solvents (e.g. dimethylsulfoxide), a variety of precursors of the general type represented by II, a variety of bases, low temperatures, and vacuum-line techniques, $CN_4$ can be obtained and isolated.

Several significant researches could be initiated with tetrazomethane. For example, this unique compound would be a superb source of carbon atoms in both the gas phase and in the condensed phase. Studies of the reactions of the carbon atoms generated from $CN_4$ would help to clarify the results obtained with recoil $C^{11}$ (2), and would probably answer the question of whether or not the reacting species from the photolysis of carbon suboxide is :CCO or a carbon atom (3). Furthermore, direct photodecomposition of $CN_4$ might yield carbon atoms in their excited singlet state, whereas decomposition via triplet sensitizer (4) would yield ground triplet carbon. A comparison of the chemical reactivities of excited singlet carbon and ground triplet would have bearing on the methylene ($:CH_2$) case,[*] since the carbon atoms, unlike methylene, can have no vibrational energy and in condensed phase would very quickly become "thermalized" (undergo relaxation) with respect to translational energy. Thus, one should be able to find reaction conditions such that the difference in reactivity could only be due to differences in spin state.

Another interesting species which might be generated from tetrazomethane is $:\overset{+}{C}H$, which has been observed in mass spectroscopy and in comet tails. In fact, a long list of interesting species, $:CN_2$, $N_2C{=}CH_2$, $:C{=}C:$, etc., which might arise from $CN_4$ can be written.

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[*] Although many workers in the methylene field have propounded the view that methylene can be generated in either an excited singlet or ground triplet state and that these states show vastly different chemical reactivities, some kineticists interpret the reactivity data in terms of an electronic state of methylene containing different amounts of vibrational energy (5).

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## PROPOSITION III

An experimental method for the accurate determination of the extinction coefficients for triplet-triplet transitions in substrates dissolved in fluid solution is proposed.

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The oscillator strengths as well as the wavelengths are important in assigning triplet-triplet transitions in organic systems. However, the determination of the extinction coefficients is difficult. McClure (1) first attempted to estimate extinction coefficients for triplet-triplet transitions. He estimated the concentration of triplets by an indirect method assuming knowledge of all processes by which the triplet state is populated and depopulated. McClure's values for the long wavelength band of the triplet-triplet absorption spectra of some of the aromatic hydrocarbons are more than an order of magnitude smaller than values reported by Craig and Ross (2) and by Porter and Windsor (3), who used an improved method. If a region of the singlet-singlet absorption spectrum is free of triplet-triplet absorption, the concentration of triplet species can be obtained by noting the decrease in intensity of the singlet-singlet absorption. Craig and Ross (2) used low intensity steady illumination to populate the triplet states and recorded the total absorption spectrum by means of a recording spectrophotometer. Under these conditions, only a very small population of triplets was achieved and the decrease in singlet-singlet absorption too small to measure accurately. Making educated guesses of an upper limit for the concentration of triplets, they were able to obtain lower limits for the extinction coefficients. Porter and Windsor (3) used the flash photolytic technique which achieves high triplet populations and thus significant decreases in the intensity of the singlet-singlet absorption. However, their procedure suffers from the fact that the double flash method of recording the total absorption spectrum must be used in which the spectrum is recorded on photographic plates. The measurement of absolute extinction curves from photographic spectra is not a very accurate procedure.

The problem of accurately determining triplet-triplet transition intensities boils down to accurately determining the concentration of triplet species under conditions where accurate photoelectric determination of the extinction can be achieved.

The following experimental method for accurately determining the concentration of triplet species in fluid solution and consequently determining triplet-triplet extinction coefficients is proposed.

One simply prepares two degassed samples in carefully matched cells. One sample contains the compound of interest dissolved in an appropriate solvent. The other sample contains, in addition, a suitable olefin quencher as described in Part I of this thesis. The sample containing the olefin is flash-photolyzed (more than one flash may be required). The extent of isomerization of the olefin gives the number and thus the concentration of triplet species produced.* The sample without the olefin is flash photolyzed in an identical way** and the extinction due to the triplet species is measured photometrically at a time close to the end of the flash.

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[*] The substrate concentration and the arrangement of the flash lamps are adjusted so that as even a distribution of triplet species as possible is achieved.

[**] The intensity of the flashes must be very nearly the same. This requirement is easily satisfied with currently available flash lamps (4).

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# PROPOSITION IV

It is proposed that the formation of the 6-hydrothyminyl radical (II) when "wet" DNA or thymine is irradiated with ultraviolet light involves proton transfer from water to the thymine radical anion. Some experiments are suggested to test this proposition.

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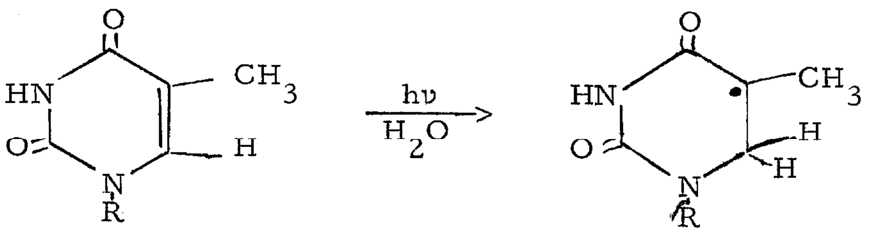
Eisinger and Shulman (1) reported unequivocal evidence (electron paramagnetic resonance (e.p.r.)) for the existence of the 6-hydrothyminal radical (II) in samples of DNA which were irradiated with X-rays or ultraviolet light at 77°K. It was shown later (2) that irradiation of thymine under the same conditions leads to the same results. Furthermore, carefully dried DNA or thymine does not give the radical product when irradiated. If the dried DNA or thymine is exposed to a moist atmosphere before

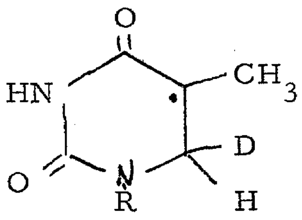


Ia R = H

Ib R = rest of DNA molecule

(II)

irradiation, the radical is easily obtained. If the dried DNA or thymine is exposed to an atmosphere of $D_2O$, the 6-deutero-radical (III) is obtained.*



III

It is proposed that the formation of II involves proton transfer from water to the thymine radical anion.

$$\begin{tikzcd} e^- + \mathrm{I} \arrow[r] & \mathrm{I}\ \text{radical anion} \arrow[d, "H_2O"] \\ & \mathrm{II} + OH^- \end{tikzcd}$$

Although thymine is photostable in fluid water (3), a closely related compound, uracil (IV) undergoes both hydration and dimerization (4). In the hydration reaction, the elements of water

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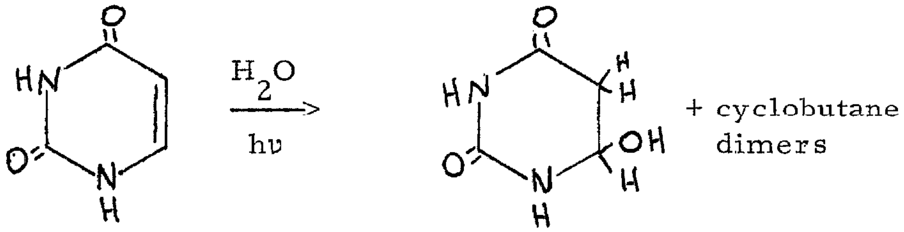
* It is conceivable that some other moiety in the DNA rather than water acts as the proton source. The formation of III would then have to be preceded by facile deuterium exchange at the proton source. Since the formation of II also occurs with pure thymine, the proton source in this case, if not water, would have to be another thymine molecule. Thus, water seems to be the most reasonable choice for a proton source.

are added to the 5- and 6-positions of the uracil to give V. Thus,



IV V

an excited state (singlet or triplet) of thymine cannot be involved in the formation of II since it is known that thymine is photostable in fluid water and does not seem to form a hydrate when irradiated in ice (3). Even if an electronically excited state of thymine does undergo reaction with water (the product being unstable at temperatures above 77°K), one would not expect the reaction to proceed by way of II, but in a manner analogous to the uracil case, i.e. addition of -OH and not -H to the 6-position. Addition of a proton to the 6-position of the thymine radical anion, on the other hand, seems reasonable.

The purines and/or cytosine could serve as excellent electron sources in the DNA, since relatively efficient photoionizations of aromatic nitrogen-heterocyclics and aromatic amines in the presence of good electron "solvents" have been observed (5,6). In the case of the pure thymine, one is forced to postulate that the electron source is another thymine molecule.[*]

One can easily evaluate this proposal by irradiating a mixture of thymine and a compound which undergoes facile photoionization (e.g. triphenylamine), in an ethylene glycol-water glass at 77°K and establishing the presence or absence of II upon irradiation of only the electron ejector. The efficiency of the purines, cytosine, and thymine as electron ejectors could be tested by irradiating a mixture of the compound and naphthalene dissolved in a glass at 77°K and searching for the naphthalene radical anion.

Although many processes involving ionization no doubt play an important role in biological radiation damage due to X-rays and other ionizing radiation, this mode of disruption of DNA has not received attention in the case of ultraviolet radiation despite the fact that ultraviolet-induced ionization has been known for two decades.

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[*] The radical cations should also be observed in the e.p.r. spectrum. In all their spectra, Eisinger and Shulman observed a reasonably intense broad resonance in addition to the resonances for II.

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# PROPOSITION V

It is proposed that the interconversion 2-methylmethylenecyclopropane (I) ⇌ ethylidenecyclopropane (II) can be realized with the use of triplet photosensitizers, the energy transfer steps involving non-vertical transitions in the cyclopropane compounds.

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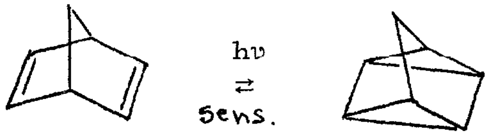
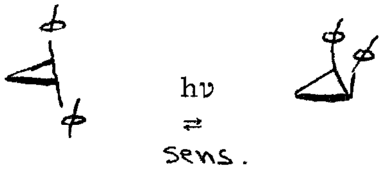
Non-vertical triplet excitation transfer (1) to saturated bonds resulting in bond cleavage currently enjoys several interesting examples (2,3). Two of these, III ⇌IV and V ⇌ VI involve an interconversion of two isomeric species. The photostationary isomer mixture, like in the case of the photosensitized cis⇌ trans isomerization of olefins (4) is a function of the sensitizer triplet excitation energy (2). However, due mainly to the inefficiency of the interconversions in III ⇌IV and V ⇌ VI and the existence of serious

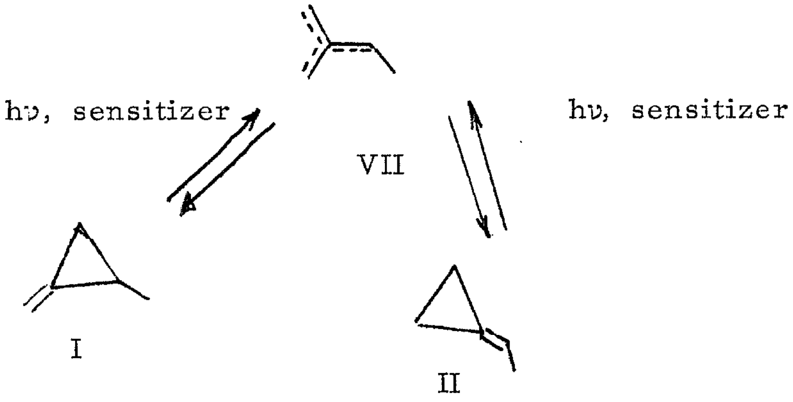


III IV



side reactions, or competing thermal reactions, photostationary isomer ratio vs. sensitizer energy plots (Saltiel plots) for these systems are obtained with difficulty and are not accurate. An extensive and accurate Saltiel plot along with good quantum yield measurements for any system involving non-vertical energy transfer would be very valuable in gaining an understanding of the characteristics of the transfer process.

It is proposed that the photosensitized interconversion 2-methylmethylenecyclopropane (I) ⇄ ethylidenecyclopropane (II) can be effected, and that the system would be ideal for determining the characteristics of non-vertical triplet energy transfer.



Both I and II have been synthesized from readily available materials (5). Mixtures can be easily and accurately analyzed by the vapor phase chromatographic technique. The compounds are interconverted at elevated temperatures but they are otherwise stable to fragmentation or polymerization even at 300°. The equilibrium constants at various temperatures and the activation energy (~40 kcal/mole) for the interconversion have been determined. At room temperature, I is more stable than II by about 3 kcal/mole (5). Thus, if non-vertical energy transfer in both I and II leads to a common intermediate, one would expect to obtain a Saltiel plot if the non-vertical excitation energies lie in a reasonable range (40-70 kcal/mole, in which range a large number of sensitizers are available). The most reasonable structure for a common intermediate is the unsymmetrical trimethylenemethane VII. This species should have a very low-lying triplet state (Figure I).

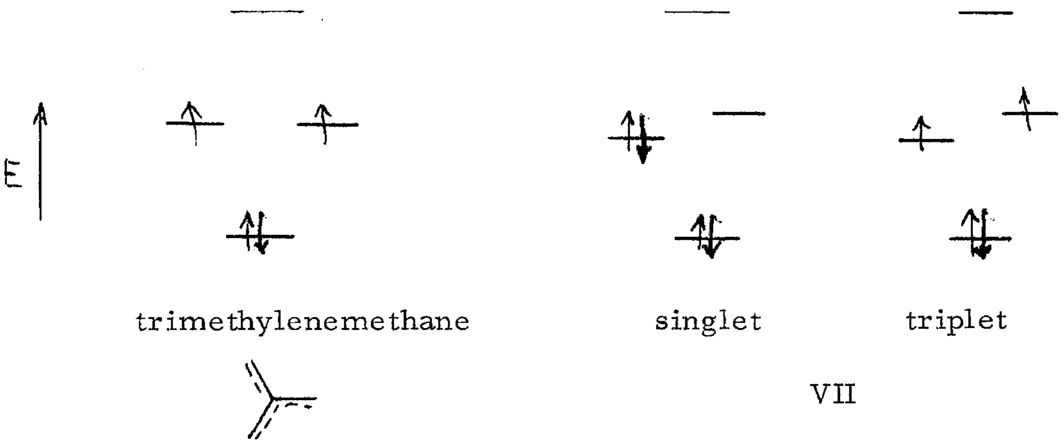


Figure I

If the activation energy for the thermal isomerization (~40 kcal/mole) approximately represents the difference between I or II and singlet VII, then the lowest triplet of VII would be expected to lie in the useful sensitizer range (40-70 kcal/mole). Finally, it is conceivable that excitation of I and II to vertical triplets might be attainable with "high energy" (75-85 kcal/mole) sensitizers, thus allowing the determination of the ratio of the rates of decay from VII to I and II.

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