Intramolecular Electronic Energy Transfer between Nonconjugated Chromophores in Some Model Compounds[1]

Angelo A. Lamola,[3] Peter A. Leermakers, Gary W. Byers, and George S. Hammond

Intramolecular transfer of both singlet and triplet electronic excitation in the three compounds 4-(1-naphthylmethyl)benzophenone (1), 1-(1-naphthyl)-2-(4-benzoylphenyl)ethane(2), and 1-(1-naphthyl)-3-(4-benzoylphenyl)propane (3) 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. Transfer of singlet excitation from the naphthalene moiety to the benzophenone group is about 90% efficient in 1, about 75% efficient in 2, and about 85% efficient in 3. The rate of the singlet energy transfer ($k \sim 10^7$–10^8 sec.$^{-1}$) is much slower than the rate of the triplet excitation transfers. The fluorescent emissions from the compounds are quite different from those from 1-methylnaphthalene, and significant bathochromic and hyperchromic effects are noted in the absorption spectra. The nature of singlet excitation transfer in the 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.

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,[4] and for certain cases theoretical treatments have been worked out in detail.[4] On the other hand, the study of intramolecular electronic energy transfer between chemically different, nonconjugated chromophores has received relatively little attention. This is an interesting area for a number of reasons. Molecular dimensions are well within the limits where some of the simple theoretical treatments break down and altogether new transfer processes might operate at such close approach of donor and acceptor. The study of excitation trans-

fer between chromophores having known fixed spatial dispositions relative to each other is also possible. Finally, these studies would find application in biologically important systems such as the nucleic acids which are composed of large numbers of nonconjugated chromophores.

A few reports of intramolecular excitation transfer between nonconjugated chromophores can be found in the literature.[5-9] The most extensive study reported is that by Schnepp and Levy[8] of singlet excitation transfer from the naphthalene group to the anthracene group in the series of compounds 4-6. The absorption spectra

1,	$n = 1$	4,	$n = 1$
2,	$n = 2$	5,	$n = 2$
3,	$n = 3$	6,	$n = 3$
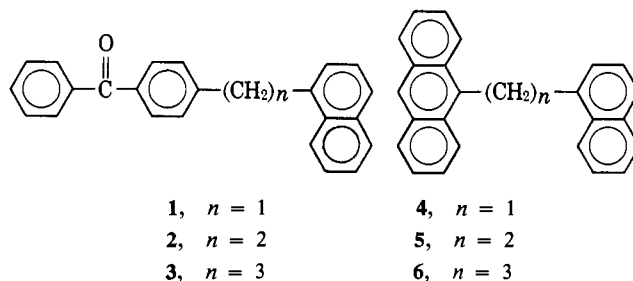
of the compounds are virtually superimposable upon the absorption spectrum of an equimolar mixture of 9-methylanthracene and 1-methylnaphthalene. The investigators reported that in glassy solution at 77°K. only anthracene fluorescence is observed from 4, 5, and 6, even if the compounds are excited at a wave length where the naphthalene moiety absorbs most of the light and under conditions where no intermolecular transfer takes place. The transfer efficiency was the same for all three compounds, 30 ± 13% of the quanta absorbed by the naphthalene group lead to the formation of excited singlet anthracene groups. The investigators pointed out that lengthening the "bridge" from one to three methylene groups does not significantly alter the distance between the chromophores because of the flexibility of the methylene chain. Thus they were not surprised that the same transfer efficiency is attained in each case and decided that the methylene bridge plays no part in the transfer. Finally, a resonance transfer mechanism was considered.

This paper describes a detailed study of intramolecular excitation transfer in the triad of compounds

(1) This paper is taken in part from the Ph.D. thesis of A. A. Lamola, California Institute of Technology, 1965. Some of the results reported herein have been previously communicated.[2]

(2) P. A. Leermakers, G. W. Byers, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2670 (1963).

(3) National Science Foundation Predoctoral Fellow, 1961–1964.

(4) (a) D. L. Dexter, *J. Chem. Phys.*, 21, 836 (1953); (b) Th. Förster, *Discussions Faraday Soc.*, 27, 7 (1959); (c) P. Livingston, *J. Phys. Chem.*, 61, 860 (1957); (d) V. L. Ermolaev, *Usp. Fiz. Nauk*, 80, 3 (1963); (e) G. Porter and F. Wilkinson, "Luminescences of Organic and Inorganic Materials," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 132–142; (f) E. Gaviola and P. Pringsheim, *Z. Physik*, 24, 24 (1924); (g) M. Kasha, *Radiation Res.*, 20, 55 (1963).

(5) G. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, 54, 640 (1958).

(6) G. Weber, *Nature*, 180, 1409 (1957).

(7) R. Bersohn and I. Isenburg, *J. Chem. Phys.*, 40, 3175 (1964).

(8) O. Schnepp and M. Levy, *J. Am. Chem. Soc.*, 84, 172 (1962).

(9) Intramolecular excitation transfer between conjugated chromophores has also received some attention.[10-12] Certain chelates of the rare earth elements are especially interesting cases.

(10) V. L. Ermolaev and A. Terenin, *J. chim. phys.*, 55, 698 (1958).

(11) G. A. Crosby, R. E. Whan, and R. M. Alire, *J. Chem. Phys.*, 34, 743 (1961).

(12) M. Bhaumik and M. A. El-Sayed, *ibid.*, in press.

1, 2, and 3 (throughout this paper this group of compounds is referred to as "our compounds"). The features of the compounds that make them especially interesting from the viewpoint of intramolecular electronic energy transfer can be seen by considering the positions of the lowest excited singlet and triplet levels of benzophenone and naphthalene (Figure 1). The lowest excited singlet level of benzophenone (B^S) lies about 3000 cm.$^{-1}$ below that of naphthalene (N^S), but the lowest triplet level of benzophenone (B^T) lies about 3000 cm.$^{-1}$ higher than that of naphthalene (N^T). Therefore, singlet energy transfer from naphthalene to benzophenone and triplet–triplet energy transfer from benzophenone to naphthalene are both feasible on energetic grounds. Furthermore, it is possible to introduce selectively the initial excitation into either chromophoric unit. Naphthalene does not absorb light of wave lengths greater than 3200 Å., while the n → π* 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 our 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. Interestingly, the first documented case of intermolecular triplet transfer[13] involved benzophenone as the donor and naphthalene as the acceptor.

Experimental

4-(1-Naphthoyl)chlorobenzene.[14] Finely powdered aluminum chloride (42 g.) was slowly added to 52 g. of p-chlorobenzoyl chloride in a 1-l. erlenmeyer flask which was warmed with a soft flame until the aluminum chloride dissolved. The deep red solution was cooled and the solid that was formed was taken back into solution by the addition of 250 ml. of carbon disulfide followed by warming on a steam bath. Naphthalene (38.4 g.) was added slowly to the solution with evolution of hydrogen chloride gas. The solution was cooled in an ice bath and the precipitate was filtered and washed twice with cold carbon disulfide. The precipitate was heated in 900 ml. of 10% aqueous sulfuric acid for 0.5 hr. on a steam bath, cooled, and extracted with ether. The ether solution was washed several times with 10% sodium bicarbonate and saturated salt solution and then dried over calcium chloride. The product distilled at 180° (1 mm.); yield 58 g. (72%).

4-(1-Naphthylmethyl)chlorobenzene. A mixture of 58 g. of 4-(1-naphthoyl)chlorobenzene, 24 g. of potassium hydroxide, 18 ml. of 85% hydrazine hydrate, and 300 ml. of ethylene glycol was added to a 500-ml. flask equipped with a thermometer well. The solution was refluxed for 6 hr. and then the lower boiling constituents were distilled off until the pot temperature reached 200°. The solution was then refluxed for 2 hr. at 200°, cooled, acidified, and extracted with ether. The ethereal solution was washed with 10% bicarbonate solution and saturated salt solution and dried over

(13) A. N. Terenin and V. L. Ermolaev, *Dokl. Akad. Nauk SSSR*, **85**, 547 (1952).
(14) This was prepared by a procedure analogous to one described by L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., p. 192.
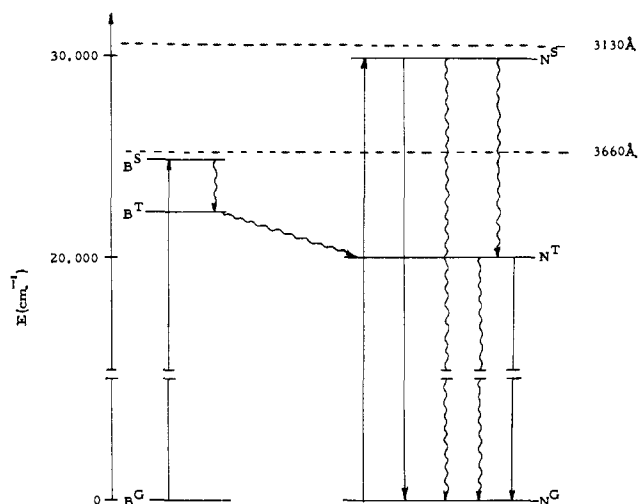

Figure 1. Excitation energies to the first excited singlet (S) and lowest triplet (T) states from the ground states (G) of benzophenone (B) and naphthalene (N) moieties in the compounds. Possible radiative transitions are represented by straight arrows, radiationless transitions by wavy arrows.

calcium chloride. The 4-(1-naphthylmethyl)chlorobenzene was vacuum distilled at 152–160° (1 mm.) after which it crystallized but was not further purified; yield 17 g. (30%).

4-(1-Naphthylmethyl)benzophenone (**1**). A mixture of 17 g. of 4-(1-naphthylmethyl)chlorobenzene, 7 ml. of dry pyridine, and 7.2 g. of cuprous cyanide was placed in a 250-ml. three-necked flask with mechanical stirrer, an air condenser, and a slow stream of nitrogen flushing the system. The mixture was heated with stirring to 230–240° in an oil bath for 40 hr. The mixture while still hot was then poured onto an ice and sodium hydroxide mixture. The aqueous solution was extracted with benzene which was filtered. washed several times with dilute hydrochloric acid and saturated salt solution, and dried over calcium chloride. The benzene was evaporated and the 4-(1-naphthylmethyl)-benzonitrile, a dark oil, was placed in a vacuum desiccator overnight. Further purification was not attempted.

Phenylmagnesium bromide was prepared in 150 ml. of anhydrous ether from 10.5 ml. of bromobenzene (0.1 mole) and 2.45 g. of magnesium metal turnings. The Grignard solution was slowly added to an ether solution of 4-(1-naphthylmethyl)benzonitrile, the entire yield from the preceding step, and then refluxed for 3 hr. The excess Grignard reagent was carefully decomposed with 20% ammonium chloride solution. The aqueous and ether layers were filtered and the magnesium hydroxide was washed twice with ether. The ether phase was concentrated to about 30 ml. and put into a 250-ml. flask. A small amount of concentrated hydrochloric acid was added to oil out the imine hydrochloride, after which most of the ether was decanted. About 150-ml. of 20% sulfuric acid and 50 ml. of toluene were added to the oil and the phases were refluxed for 8 hr. The heterogeneous mixture was then cooled and ether was added to dilute the toluene layer. The organic layer was then washed twice with 10% bicarbonate and then with saturated salt solution. The toluene–ether solution was evaporated, leaving a

dark oil which was dried in a vacuum desiccator. The 4-(1-naphthylmethyl)benzophenone was purified by column chromatography on alumina giving yellow crystals. Recrystallization from methanol gave white needle-like crystals, m.p. 80.5°; yield 7 g. (33%).

Anal. Calcd. for $C_{24}H_{18}O$: C, 89.6; H, 5.6. Found: C, 89.4; H, 5.8.

1-(1-Naphthyl)-2-(4-chlorophenyl)ethane. An ether solution of 22.5 g. of 1-naphthylmethyl chloride, obtained from a lithium aluminum hydride reduction of 1-naphthaldehyde with subsequent reaction of the alcohol with thionyl chloride, was added slowly to 3.10 g. of magnesium in 100 ml. of ether. After formation of the Grignard reagent was completed, 17.5 g. of 4-chlorobenzonitrile in 50 ml. of ether was added. After the initial reaction, the solution was refluxed overnight and then decomposed with 20% ammonium chloride solution. The magnesium hydroxide was washed twice with ether. The ether phases were combined, concentrated to about 50 ml., and placed in a 500-ml. flask. Concentrated hydrochloric acid was added to oil out the imine hydrochloride, whereupon the ether was decanted and 250 ml. of 20% sulfuric acid and 100 ml. of toluene were added. The mixture was refluxed for 14 hr. and cooled, and the toluene layer was diluted with ether. The organic layer was washed with 10% bicarbonate and saturated salt solution and then evaporated leaving 1-naphthyl(4-chlorobenzoyl)methane, a slightly yellow solid.

The entire yield of 1-naphthyl(4-chlorobenzoyl)methane was transferred to a 500-ml. round-bottom flask equipped with a thermometer well. Ethylene glycol (200 ml.), 11.8 ml. of 85% hydrazine hydrate, and 15 g. of potassium hydroxide were added. The reduction and work-up were carried out in a fashion analogous to the reduction of 4-(1-naphthoyl)chlorobenzene previously mentioned. The product was vacuum distilled at 178° (1 mm.) giving a colorless oil.

1-(1-Naphthyl)-2-(4-benzoylphenyl)ethane (2). At this point this synthesis is completely analogous to that of 4-(1-naphthylmethyl)benzophenone. The 1-(1-naphthyl)-2-(4-cyanophenyl)ethane was synthesized analogously to 4-(1-naphthylmethyl)benzonitrile by using 10.0 g. of 1-(1-naphthyl)-2-(4-chlorophenyl)ethane, 4.85 g. of cuprous cyanide, and 5 ml. of pyridine. Likewise, the 1-(1-naphthyl)-2-(4-cyanophenyl)ethane was also allowed to react with 0.1 mole of phenylmagnesium bromide with the same work-up. The 1-(1-naphthyl)-2-(4-benzoylphenyl)ethane was purified on an alumina column giving a slightly yellow oil, which after a molecular distillation was colorless.

Anal. Calcd. for $C_{25}H_{20}O$: C, 89.5; H, 5.9. Found: C, 89.8; H, 5.8.

1-(1-Naphthyl)-3-(4-chlorophenyl)propane. The preparation of this compound was analogous to that of 1-(1-naphthyl)-2-(4-chlorophenyl)ethane. 2-(1-Naphthyl)chloroethane (55 g.), obtained from a lithium aluminum hydride reduction of ethyl (1-naphthyl)-acetate with subsequent reaction of the alcohol with thionyl chloride, was allowed to react with 7.25 g. of magnesium metal turnings in 200 ml. of ether. This Grignard reagent was then added to 43 g. of 4-chlorobenzonitrile. The 1-(1-naphthyl)-2-(4-chlorobenzoyl)-ethane was distilled at 204° (1 mm.). The Wolff–

Kischner reaction was then run on the 1-(1-naphthyl)-2-(4-chlorobenzoyl)ethane just as it was on 1-naphthyl-(4-chlorobenzoyl)methane but using 38 g. of 1-(1-naphthyl)-2-(4-chlorobenzoyl)ethane, 20 ml. of ethylene glycol, 15 g. of potassium hydroxide, and 11.5 ml. of 85% hydrazine hydrate. The 1-(1-naphthyl)-3-(4-chlorophenyl)propane was distilled at 181° (1 mm.) and was a clear oil.

1-(1-Naphthyl)-3-(4-benzoylphenyl)propane (3). The 1-(1-naphthyl)-3-(4-cyanophenyl)propane was prepared by a procedure analogous to 4-(1-naphthylmethyl)-benzonitrile using 23 g. of 1-(1-naphthyl)-3-(4-chlorophenyl)propane, 9 g. of cuprous cyanide, and 10 ml. of pyridine. The 1-(1-naphthyl)-3-(4-cyanophenyl)propane was distilled at 214° (1 mm.) and it solidified but was not further purified; yield 13.5 g. (61%).

The 1-(1-naphthyl)-3-(4-cyanophenyl)propane was treated with phenylmagnesium bromide (0.11 mole). After a work-up similar to that for 4-(1-naphthyl-methyl)benzophenone, the 1-(1-naphthyl)-3-(4-benzoyl-phenyl)propane was purified on an alumina column giving a slightly yellow oil, which after a molecular distillation was clear.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.1; H, 6.3. Found: C, 88.9; H, 6.3.

4-(1-Naphthylmethyl)benzhydrol (1-Alcohol). 4-(1-Naphthylmethyl)benzophenone dissolved in ether was reduced to the corresponding alcohol with lithium aluminum hydride. The mixture was worked up in the usual manner and recrystallized from methanol, m.p. 68–69°. The yield was essentially quantitative. N.m.r., infrared, and ultraviolet analyses, as well as the method of synthesis, confirmed the identity of the compound.

1-Methylnaphthalene (Calbiochem, reagent) was passed through a column of neutral alumina just prior to use. *4-Methylbenzophenone* (Eastman White Label) was twice recrystallized from pentane. It melted at 59–60° (uncor.). Benzophenone (Matheson Coleman and Bell, reagent grade) was recrystallized twice from diethyl ether. It melted at 48–48.5° (uncor.). *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. The EPA formed a clear glass at 77°K. which showed no emission when irradiated with light of 3130-Å. wave length.

Emission Spectra. A photoelectric spectrophosphorimeter consisting of a Jarrell-Ash $^1/_2$-m. Ebert scanning grating monochromater (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 (freeze–thaw–pump method) 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 to 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 phos-

phoroscope was removed. All spectra were recorded at a scanning rate of 50 Å./min. A correlation of scanning rate and recorder chart speed allowed wave length determination (± 5 Å.) directly from the recorded spectra. The wave length indicator on the monochromater was calibrated from time to time using the mercury lines as standards. None of the spectra was corrected for the spectral sensitivity of the apparatus.

The samples were carefully prepared solutions in EPA. All the concentrations reported in this paper are room temperature concentrations. The concentrations at 77°K. are higher since the EPA contracts to about $2/3$ the room temperature volume when frozen to 77°K.

Piperylene Photostationary States.[15] Carefully prepared samples containing sensitizer (**1**, **2**, or **3**) and either *cis*- or *trans*-piperylene in Phillips research grade benzene were loaded into 13 × 100 mm. Pyrex test tubes. The samples were degassed by the freeze-pump–thaw method and sealed under vacuum. The samples were irradiated with light of wave length 3660 Å. until a photostationary isomer mixture was achieved. The composition at photostationary state was determined by vapor phase chromatography using a 20-ft. × 0.25-in. column packed with 15% 1,2-bis(2-cyanoethoxy)ethane on Chromosorb P (45–60 mesh) maintained at room temperature.

Triplet Yields.[16] Thoroughly degassed matched samples containing the sensitizer in question and 0.05 *M* pure *cis*-piperylene in Phillips research grade benzene in sealed Pyrex tubes were irradiated with 3130-Å. light along with identically prepared samples using benzophenone as sensitizer in such a manner that all samples absorbed the same amount of light. Irradiation times were such as to effect 2–5% conversion of the *cis*-piperylene to the *trans* isomer. The conversions were determined by the vapor phase chromatographic method using a 20-ft. × 0.25-in. column packed with 15% 1,2-bis(2-cyanoethoxy)ethane in Chromosorb P (45–60 mesh) maintained at room temperature employing a Lenco Model 15B fractometer equipped with a hydrogen flame detector. The ratio of the conversion in the sample containing the sensitizer in question to that containing benzophenone (triplet yield 1.00[16]) gives the triplet yield for that sensitizer.

Results

Several different kinds of measurements were obtained in order to elucidate the modes and efficiencies of excitation transfers in the compounds. These included determination of absorption and emission spectra, measurement of emission lifetimes, characterization of the compounds as triplet sensitizers in the isomerization of olefins, and measurements of the yields of quenchable triplets upon optical excitation of the compounds. 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 mixture of 1-methylnaphthalene and 4-methylbenzophenone in cyclohexane exhibits an absorption spectrum (Figure 2)

(15) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).
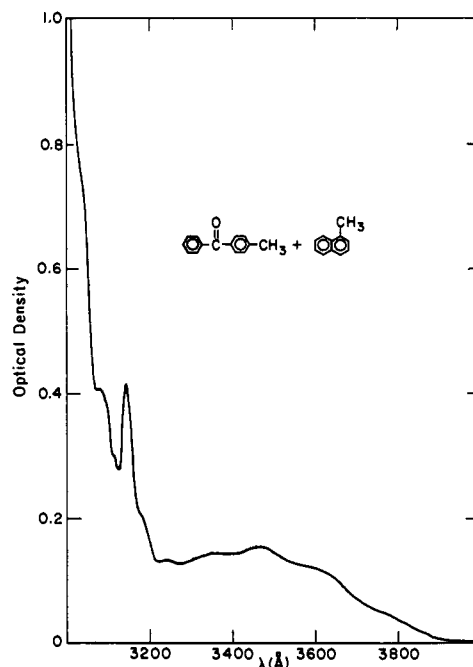(16) A. A. Lamola and G. S. Hammond, in preparation.

Figure 2. Absorption spectrum of an equimolar mixture of 1-methylnaphthalene and 4-methylbenzophenone in cyclohexane.

exactly equal to the sum of the spectra of the constituents recorded alone. Figures 3, 4, and 5 show the absorption spectra of **1**, **2**, and **3**, respectively. Difference spectra, computed by subtracting the absorption of the equimilar mixture of 1-methylnaphthalene and 4-methylbenzophenone from each of the other spectra, are also shown (dashed lines). These small but important spectral changes may be due chiefly to long-range exciton interactions between the excited states of the chromophoric groups.[17] Such interactions are believed to result in excitation delocalization responsible for wave length shifts (bathochromism and hypsochromism) found in dye aggregates and molecular crystals,[18,19] and intensity changes (hypochromism and hyperchromism) as found in molecular aggregates, in double-chain polynucleotides,[20] and in helical polypeptides.[21]

The absorption spectra of **1** and **3** do not differ very much from that of an equimolar mixture of 4-methylbenzophenone ($\epsilon_{3130\text{Å}} \approx 70$) and 1-methylnaphthalene ($\epsilon_{3130\text{Å}} \approx 300$). The difference spectra for **1** and **3** are similar and could result from modification of the local interaction of the methyl group with the naphthalene nucleus by introduction of the larger substituents for hydrogen; alternatively, there may be new transitions due to interactions between higher excited states of the unsaturated groups. At any rate, the difference spectra are not very "intense" at 3130 Å. and so it is safe to say that use of excitation of 3130-Å. wave length leads predominantly (60–80%) to excitation of the naphthalene-like chromophores in **1** and **3**.

(17) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963.
(18) D. P. Craig, *J. Chem. Soc.*, 2302 (1955).
(19) M. Kasha, *Rev. Mod. Phys.*, **31**, 162 (1959).
(20) I. Tinoco, *J. Am. Chem. Soc.*, **82**, 4785 (1960); *ibid.*, **83**, 5047 (1961); W. Rhodes, *ibid.*, **83**, 3609 (1961).
(21) I. Tinoco, A. Halpern, and W. T. Simpson, "Polyamino Acids, Polypeptides, and Proteins," M. A. Stehman, Ed., University of Wisconsin Press, Madison, Wis., 1962, p. 147.
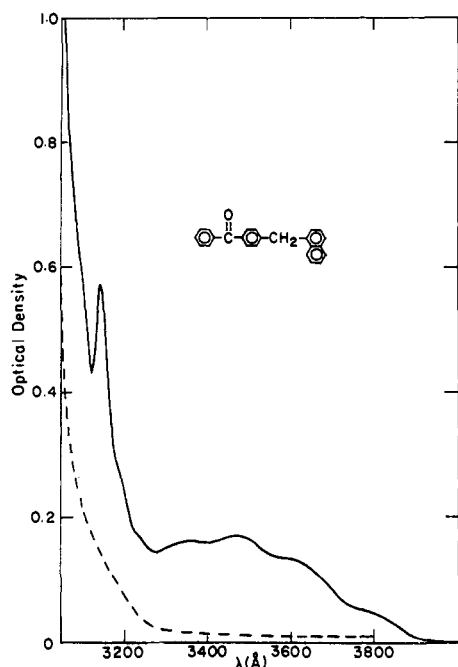
Figure 3. Absorption spectrum of 1 in cyclohexane (dashed line is difference between this spectrum and that of an equimolar mixture of 1-methylnaphthalene and 4-methylbenzophenone).

Figure 5. Absorption spectrum of 3 in cyclohexane (dashed line is difference between this spectrum and that of an equimolar mixture of 1-methylnaphthalene and 4-methylbenzophenone).
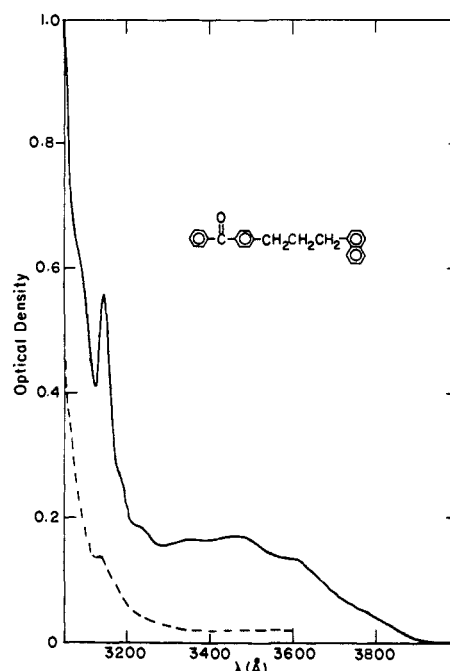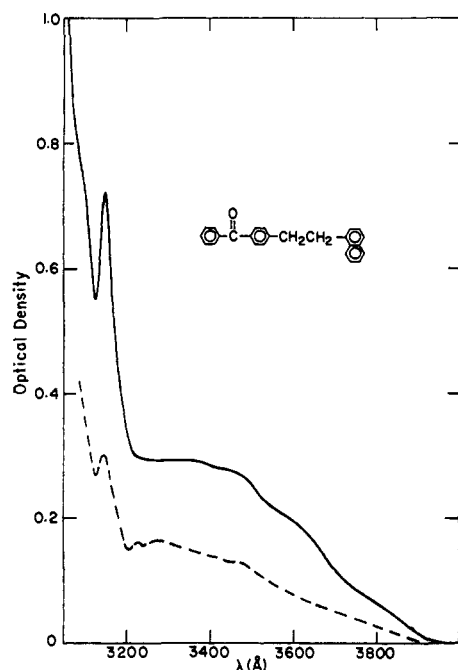

Figure 4. Absorption spectrum of 2 in cyclohexane (dashed line is difference between this spectrum and that of an equimolar mixture of 1-methylnaphthalene and 4-methylbenzophenone).

The absorption spectrum of 2 shows a significant hyperchromicity relative to that of the equimolar mixture of 4-methylbenzophenone and 1-methylnaphthalene. As can be seen in the difference spectrum, both the n → π* transition in the benzophenone chromophore and the lowest transition in the naphthalene group show an intensity increase of about 50%. Here, too, it is safe to say that most of the light of 3130-Å. wave length absorbed by 2 is absorbed by the naphthalene moiety.

The interactions leading to the differences in the absorption spectra of our compounds are expected from theory[20,21] to be extremely dependent on the geometries of the molecule. Although information concerning the natures and directions of polarization of some of the transitions in naphthalene and benzophenone is available,[22-24] nothing certain can be said about the relative orientations of the chromophores in the compounds. Consequently, unequivocal specification of the specific interactions that are involved is not possible at this time. Some observations concerning the geometries of the compounds 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 compounds. In an attempt to obtain information about the geometries, molecular models (Leybold models) were constructed. No conformations significantly different from those possessed by the models of 1 and 3 were found in the model of 2. The models show that 3 can "explore" more intermediate conformations than can 2, and in turn 2 can "explore" more than 1. What the preferred conformations are in each case is not obvious either.

Simple steric considerations would suggest that the *trans* conformer, 7, should be favored. However, routine interpretation of the exalted absorption would suggest the prevalence of other conformations, such as *gauche* forms like 8 which allow something approaching "face-to-face" interaction of the unsaturated groups. Similar relative orientations of the groups can be accomplished in 3 but this would of course sacrifice more in the way of normally unrestricted motion in the longer methylene chain.

(22) M. A. El-Sayed, *J. Chem. Phys.*, 36, 1943 (1962).
(23) D. S. McClure and P. L. Hanst, *ibid.*, 23, 1772 (1955).
(24) D. S. McClure, *ibid.*, 24, 1 (1956).

Structures 7 and 8 at top left.
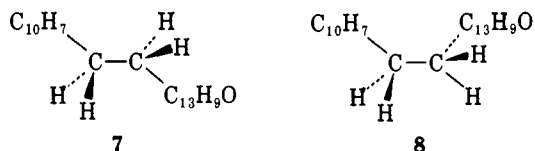
Emission Spectra and Lifetimes. The only emission[25] detected from an equimolar (5×10^{-3} M) mixture of 1-methylnaphthalene and 4-methylbenzophenone under excitation with 3660-Å. light in a rigid glass was phosphorescent emission from 4-methylbenzophenone (Figure 6). This result indicates that at the concentrations employed, there is little, if any, intermolecular transfer of triplet excitation. The phosphorescence spectra of 1, 2, and 3, however, are almost identical with that of 1-methylnaphthalene even when only the benzophenone chromophore is excited (3660 Å.). No emission characteristic of 4-methylbenzophenone was observed from 1, 2, and 3 under conditions where 0.1% emission from the benzophenone moiety could have been detected. Figure 6 shows the phosphorescence spectrum of 1 along with those of 1-methylnaphthalene and the equimolar mixture of the model compounds.

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 7. At this wave length, the ratio of the number of quanta absorbed by the 1-methylnaphthalene to the number absorbed by the 4-methylbenzophenone is about 4:1. However, since the quantum yield of phosphorescence from 1-methylnaphthalene is very low ($\sim$0.05) and that of 4-methylbenzophenone is very high (probably >0.8),[26] the phosphorescent emission from the latter dominates the long wave length region. The short wave length region shows the fluorescence spectrum of the 1-methylnaphthalene. The slight difference between this spectrum (Figure 7) and that of 1-methylnaphthalene in the absence of the 4-methylbenzophenone (Figure 8) is attributed to a small amount of reabsorption ("trivial" radiative transfer) by the 4-methylbenzophenone. A calculation of the maximum amount of reabsorption expected (considering concentration, sample size, geometry of the system, etc.) gave between 0 and 10%, depending on the wave length of the fluorescent emission.

The total emission spectrum of 1 (10^{-3} M) is shown in Figure 9. The short wave length (3150–4500 Å.) emission assigned as fluorescence from the naphthalene chromophore is very weak compared with that recorded from the equimolar mixture of 4-methylbenzophenone and 1-methylnaphthalene (Figure 7). Furthermore, the fluorescence spectrum of 1 appears to be quite different from that of 1-methylnaphthalene (Figure 8). The carbonyl group of 1 was reduced using lithium aluminum hydride to give the 1-alcohol. The total

1-alcohol

(25) All emission spectra reported here were obtained from samples dissolved in EPA glass at 77°K.
(26) E. H. Gilmore, G. E. Gibson, and D. S. McClure, *J. Chem. Phys.*, **20**, 829 (1952); *ibid.*, **23**, 399 (1955); V. L. Ermolaev, *Opt. Spectry.* (USSR), **11**, 266 (1961).
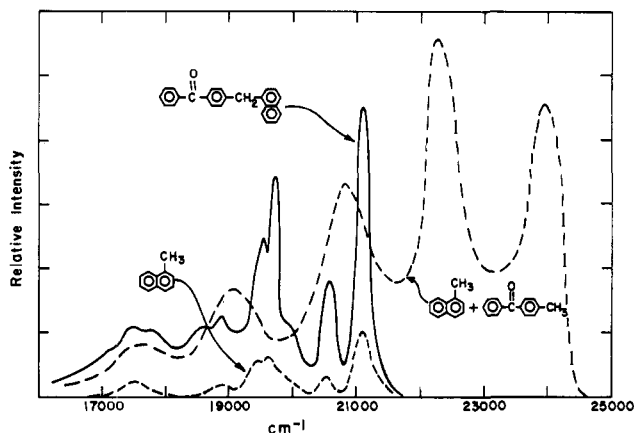

Figure 6. Comparison of phosphorescence spectrum of 1 with those of model compounds.
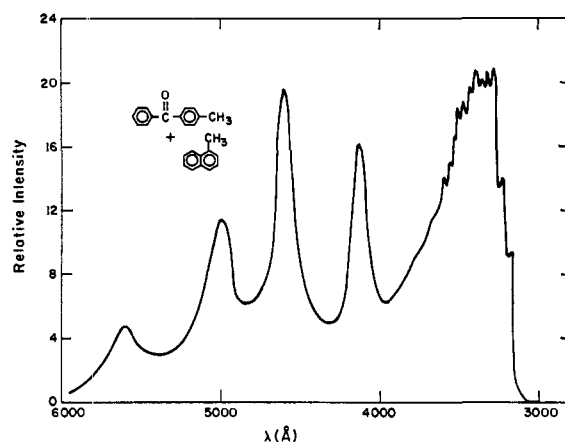

Figure 7. Emission spectrum of an equimolar (5×10^{-3} M) mixture of 1-methylnaphthalene and 4-methylbenzophenone in EPA glass under 3130-Å. irradiation.

emission spectrum of this compound (Figure 10) is very similar to that of 1-methylnaphthalene.

Compounds 2 and 3 (Figures 11 and 12) show complex total emission spectra. In both cases the high-frequency emission, attributed to fluorescence from the naphthalene units, is stronger than from 1. There are other even more striking differences between the spectra of 2 and 3 and those of 1 and the other reference compounds. Although the positions of the shortest wave length bands for the fluorescent emissions from 1-methylnaphthalene and our compounds are nearly the same and all of the compounds exhibit a maximum between 3300 and 3400 Å., our compounds show another maximum near 4000 Å. The general shapes of the emission from the compounds in the 3300–3500-Å. region are about what would be expected if absorption of naphthalene group fluorescence by the benzophenone chromophores were occurring. The n → π* absorption band of benzophenone extends from 3100 to 3900 Å.

The naphthalene-like phosphorescence from the compounds excited with 3130-Å. light is more intense than that from 1-methylnaphthalene or the 1-alcohol. The approximate relative phosphorescent intensities are for 1-methylnaphthalene:1:2:3, 5:10:7:9. For a comparison of the phosphorescent intensities to be mean-
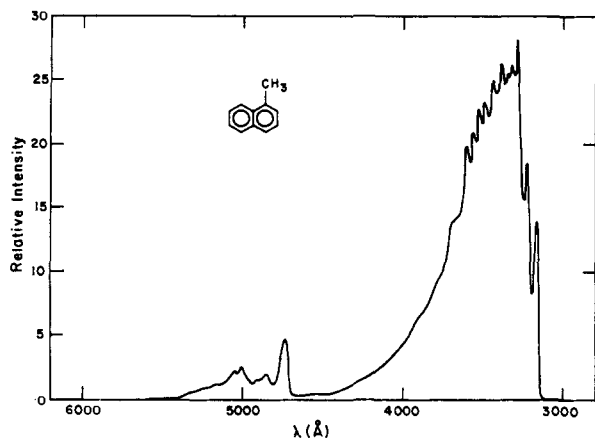
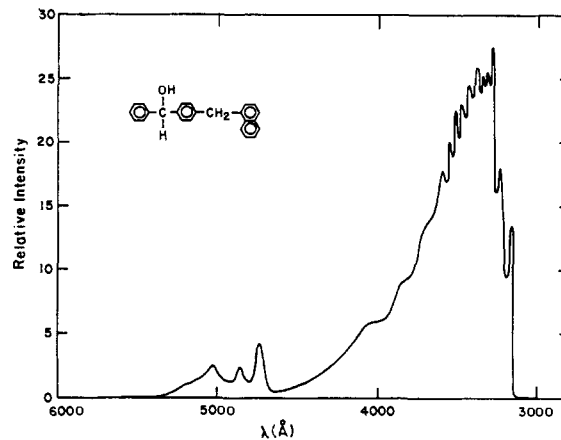Figure 8. Emission spectrum of 1-methylnaphthalene.
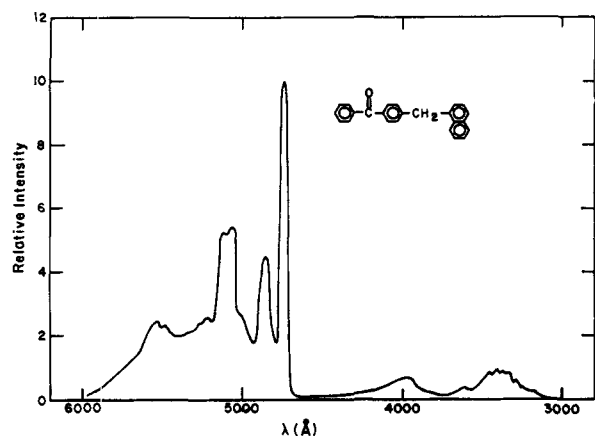

Figure 10. Total emission spectrum of 1-alcohol.

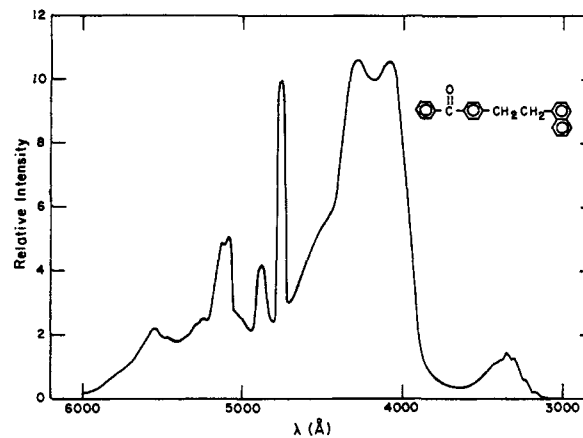Figure 9. Total emission spectrum of **1**.

Figure 11. Total emission spectrum of **2**.

ingful, the rates of radiative and nonradiative decay (sum of these rates $= 1/\tau_p$) of the naphthalene triplets must be nearly the same. The measured phosphorescent lifetimes (τ_p) for 1-methylnaphthalene, **1**, **2**, and **3** are nearly the same (2.5 ± 0.2 sec.). Thus, comparison of the intensities of the phosphorescence spectra of these compounds recorded under similar conditions is a good indication of the relative numbers of triplets produced upon excitation of the compounds.

Photosensitized Isomerization of the Piperylenes. The compounds were used as sensitizers in the photosensitized *cis* → *trans* isomerization of the piperylenes (1,3-pentadienes).[14] The isomer ratio at photostationary state is a function of the lowest triplet-state energy of the sensitizer, and so the sensitizer characteristics of our compounds in this regard would be a chemical method of detecting intramolecular triplet energy transfer. Furthermore, the use of high concentrations of piperylene might lead to quenching of the benzophenone moiety triplets before intramolecular energy transfer occurred, demonstrating the existence of the benzophenone-like triplets and yielding information about the rate of the intramolecular excitation transfer. In these experiments exciting light absorbed only by the benzophenone groups was used. The results of these experiments are shown in Table I.

Yields of Quenchable Triplets. The yields of triplets produced upon excitation of our compounds including 1-alcohol and 1-methylnaphthalene were determined
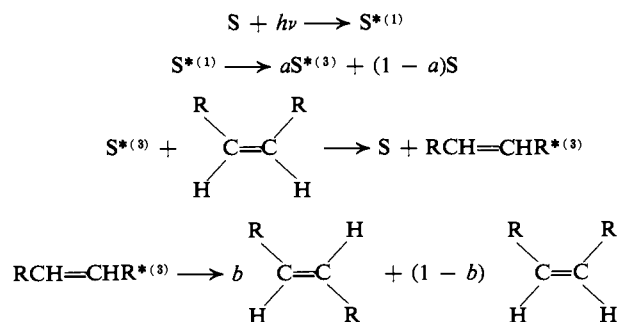
Table I. Photostationary Isomer Ratios in the *cis* ⇌ *trans* Isomerization of the Piperylenes[a]

Sensitizer	E_T, cm.$^{-1b}$	Pipery-lene concn., M	$(t/c)_{pss}{}^c$
Benzophenone	32,950	0.2	1.25
Naphthalene[d]	21,280	0.2	2.18
1-Methyl-naphthalene[d]	21,044	0.2	2.16
1	21,097	0.2	2.03
		0.05	2.10
2	21,008	0.2	1.99
		0.05	2.11
3	21,008	0.2	1.97
		0.05	2.07

[a] Benzene solution at room temperature; 3660-Å. excitation. [b] Lowest triplet level (0–0' band position in phosphorescence spectrum). [c] *trans/cis* at photostationary state; accuracy ± 0.03. [d] 3130-Å. excitation.

by using the triplet counting method developed by Hammond and Lamola.[15] In brief, the method consists of measurement of the quantum yield at low conversion of a suitable *cis* ⇌ *trans* isomerization

reaction using the compound in question as a photo-sensitizer (S). The following equations illustrate the principles.

$$S + h\nu \longrightarrow S^{*(1)}$$

$$S^{*(1)} \longrightarrow aS^{*(3)} + (1-a)S$$

$$S^{*(3)} + \underset{H}{\overset{R}{\diagdown}}C{=}C\underset{H}{\overset{R}{\diagup}} \longrightarrow S + RCH{=}CHR^{*(3)}$$

$$RCH{=}CHR^{*(3)} \longrightarrow b\ \underset{H}{\overset{R}{\diagdown}}C{=}C\underset{R}{\overset{H}{\diagup}} + (1-b)\ \underset{H}{\overset{R}{\diagdown}}C{=}C\underset{H}{\overset{R}{\diagup}}$$

With suitably chosen systems, the efficiency of transfer of triplet excitation can be made 100% by using moderately high concentrations of the olefin. The decay ratios $[b/(1-b)]$ for a number of such substrates have been accurately determined.[14] Consequently, there is a simple relationship between the measured quantum yields and a, the efficiency of triplet formation: $a = \phi_{c \to t}/b$.

In this case, cis-piperylene was the olefin used, and the triplet yields were measured relative to that for benzophenone which is 1.00.[15] The results using exciting light of both 3130- and 3660-Å. wave length are listed in Table II.

Table II. Yields of Triplets[a]

Sensitizer	Concn., M	Excitation 3130 Å.	Excitation 3660 Å.
Benzophenone	0.05	[1.00]	[1.00]
4-Methylbenzophenone	0.05	1.00	1.00
1-Methylnaphthalene	0.0125	0.48	...
1	0.05		1.00
	0.01	0.98	
2	0.05		0.99
	0.01	0.80	
3	0.05		1.01
	0.01	0.94	
1-alcohol	0.0125	0.58	...

[a] Relative to benzophenone; yield of triplets upon excitation of benzophenone is 1.00[15]; precision is ±5%; benzene solution at room temperature; cis-piperylene (0.05 M in all cases) quencher.

Discussion

Triplet–Triplet Excitation Transfer. The fact that no emission characteristic of benzophenone is observed from our compounds and only intense naphthalene-like phosphorescence is observed even when the exciting light is absorbed only by the benzophenone groups 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). The experiments involving the photostationary states of piperylenes (Table I) clearly show, as do the phosphorescence spectra, that although only the benzophenone groups absorbed the exciting light, efficient energy transfer occurs resulting in localization of the triplet excitation
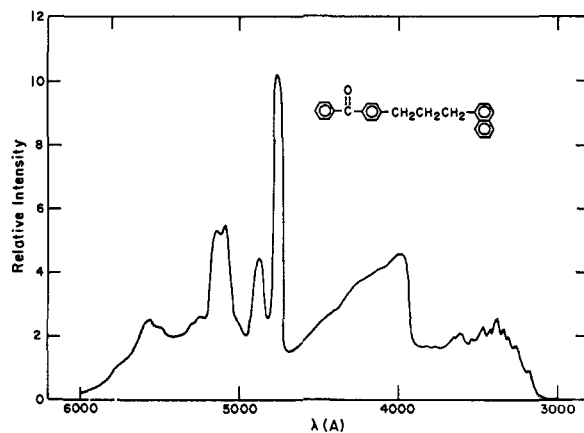

Figure 12. Total emission spectrum of 3.

in the naphthalene moiety. However, a close look at the data reveals that at the high piperylene concentration used, there may be some interception of benzophenone-like triplets. This results in $(t/c)_{pss}$ values lower than those expected if only naphthalene triplets were quenched (2.16–2.18). The $(t/c)_{pss}$ values using our 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 III). As expected, lowering the piperylene concentration to 0.05 M results in less efficient interception of benzophenone chromophore triplets and higher $(t/c)_{pss}$ values, 2.07–2.11. *These results clearly demonstrate the intermediacy of the benzophenone group triplet in the energy-transfer scheme.*

Table III. Interception of Benzophenone Chromophore Triplets[a]

Sensitizer	Concn. of pipery-lene, M	t/c_{pss}	% benzo-phenone moiety triplets quenched[b]
4-Methylbenzophenone	...	1.25	[100]
1-Methylnaphthalene	...	2.16	[0]
1	0.20	2.03	9
	0.05	2.10	3
2	0.20	1.99	11
	0.05	2.11	3
3	0.20	1.97	13
	0.05	2.07	5

[a] Benzene solution at room temperature; 3660-Å. excitation. [b] Calculation of these values is based on the mechanism for the photosensitized isomerization as given by G. S. Hammond, et al., J. Am. Chem. Soc., **86**, 3197 (1964). For a single sensitizer, the piperylene photostationary state isomer ratio is independent of the piperylene concentration.

The yields of triplets with 3660-Å. excitation (Table II) show that every quantum absorbed by a benzophenone chromophore in compounds **1**, **2**, and **3** results in the formation of a quenchable triplet. Combining these data with the results discussed above leads to the following conclusion. *Irradiation of our compounds with light of 3660-Å. wave length leads to excitation of the benzophenone group to its lowest n → π* 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.*

The phosphorescent lifetime (τ_p) of benzophenone is 5×10^{-3} sec. (EPA at 77°K.).[25] Since no emission characteristic of benzophenone is observed from our compounds, triplet excitation transfer must occur at the rate of at least $1000 \times 1/\tau_p = 2 \times 10^5$ sec.$^{-1}$. However, the data from the piperylene quenching experiments demand a much larger transfer rate. Transfer of triplet excitation from benzophenone to both *cis*- and *trans*-piperylene occurs at the diffusion-controlled rate.[14] If quenching of the benzophenone-like triplets of the compounds by piperylene 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 the ketonic triplets that must be intercepted to account for the observed photostationary states are listed in Table III. 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 intermolecular transfer of the high-energy excitation to piperylene. In the presence of 0.05 M piperylene, the intramolecular transfer is 20 to 30 times faster than the intermolecular quenching. Since k_q is about 10^{10} l. mole^{-1} sec.$^{-1}$, the intramolecular triplet transfer rate is about $1-2 \times 10^{10}$ sec.$^{-1}$. However, the calculated fractions of benzophenone chromophore triplets intercepted are very close to the fractions of benzophenone groups 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.[27] One might conclude, then, that the intramolecular transfer rate is greater than 10^{10} sec.$^{-1}$, and so only those piperylene molecules that are nearest neighbors to the benzophenone moiety at the time it reaches the triplet state are effective in quenching. This picture would make both intramolecular transfer and intermolecular transfer to nearest neighbors much faster than any diffusive displacements. On the basis of the chemical quenching experiments one can conclude that *the rate of triplet excitation transfer in compounds 1, 2, and 3 is at least* 10^{10} *sec.*$^{-1}$ *and that the transfer rate must be nearly the same for all three cases.*

The triplet excitation transfer might occur by an exchange interaction involving overlap of electron clouds of the two unsaturated groups, by excitation migration not involving overlap (resonance transfer), or because of interactions involving the methylene bridge. Intermolecular triplet excitation transfer from benzophenone to naphthalene in solution probably involves an exchange mechanism.[4d,e] The radius of the "sphere of action quenching"[28] for the benzophenone-naphthalene system was estimated to be about 13 Å.[4d] Measurements on the molecular models of the compound showed that the distance between the carbonyl carbon atom and the center of the naphthalene group is at most about 10 Å. in all three cases. Consequently,

on this basis, the exchange mechanism can operate in these compounds. Using Förster's model, it can be calculated that the distance required between the centers of a benzophenone molecule and a naphthalene molecule to obtain 50% efficient triplet excitation transfer *via* a dipole–dipole interaction is 1 Å.[4c] However, the approximations contained in the Förster model breakdown at much larger distances. Furthermore, at the close approach of chromophores as found in the compounds, higher multipole interactions could contribute significantly to exciton migration. Consequently, an exciton mechanism cannot be discounted at this time.

It is not likely that the methylene bridges are involved to any significant extent in the transfer of triplet excitation in any of the compounds since an expected large dependence of the transfer rate on the number of methylene units is not observed.[29] The triplet excitation transfer rates are very nearly the same in the three cases.

Intermolecular transfer of triplet excitation in fluid solution at room temperature by the exchange mechanism can occur at the diffusion-controlled rate, that is, upon every collisional encounter. Encounter times in typical organic solvents at room temperature are on the order of 10^{-11} sec.[32] or longer. Thus, the exchange mechanism can account for the observed rate of triplet excitation transfer in our compounds. No estimate of the rate of transfer by an exciton mechanism can be made.

Finally, theoretical calculations[33] predict that the excitation energy of the second triplet state of naphthalene lies about 300 cm.$^{-1}$ higher than the lowest benzophenone triplet state. Thus, triplet transfer from benzophenone to naphthalene is directly to the lowest naphthalene triplet state.

Singlet Excitation Transfer. The fluorescent emissions from compounds 1, 2, and 3 (Figures 6, 8, and 9) using 3130-Å. exciting light are very much less intense than that observed from 1-methylnaphthalene (Figure 5) or the equimolar mixture of 4-methylbenzophenone and 1-methylnaphthalene under the same conditions. Yet, the absorption spectra of the compounds reveal that most (70–80%) of the light of 3130-Å. wave length is absorbed by the naphthalene moieties. That the decrease in fluorescent intensities in the compounds can be attributed to intramolecular singlet excitation transfer from the naphthalene groups to the benzophenone chromophores is evidenced by the concomitant increase in the phosphorescent intensities. In the previous section, it was shown that in all of our compounds excitation of the benzophenone groups leads to totally efficient formation of naphthalene-like triplets. Thus, singlet excitation transfer from the naphthalene chromophores to the benzophenone groups should lead to an increase in the intensity of phosphorescence from the naphthalene chromophore. From the total emis-

(27) G. S. Hammond and H. P. Waits, *J. Am. Chem. Soc.*, 86, 1911 (1964).

(28) 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.

(29) A rough calculation based on perturbation theory[30,31] showed that increasing the bridge length by one methylene group should reduce the rate of transfer by a factor of 20 if the transfer arises because of chromophore-bridge interactions.

(30) H. M. McConnell, *J. Chem. Phys.*, 35, 508 (1961).

(31) H. Sternlicht, G. C. Nieman, and G. W. Robinson, *ibid.*, 38, 1326 (1963).

(32) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(33) R. Pariser, *J. Chem. Phys.*, 24, 250 (1956).

sion spectra it can be seen, at least qualitatively, that the decrease in fluorescent intensities is compensated by an increase in phosphorescence intensity.[34] The efficiency of formation of naphthalene-like triplets in the compounds upon irradiation with 3130-Å. light (Table II) strongly indicates that singlet excitation transfer operates. Assuming 70–80% of the light is absorbed by the naphthalene moiety and a 50% intersystem crossing efficiency, 35–40% of the quanta absorbed would become triplets if the excitation stayed in the naphthalene nucleus. An additional 20–30% yield of triplets would be expected to arise from light absorbed directly by the benzophenone groups so the total efficiency of formation of triplets would be 55–70%. But the triplet counting data for 3130-Å. excitation (Table II) indicate 98% for 1, 80% for 2, and 94% for 3.[35] Thus, unless the benzophenone groups exert some strange, long-range control over intersystem crossing in the naphthalene chromophores, the high yield of triplets under 3130-Å. excitation can only be accounted for if singlet energy is transferred from the naphthalene group to the benzophenone group. The fact that the carbonyl function is necessary for this decrease in fluorescent intensities and increase in phosphorescent intensities is indicated by the total emission spectrum (Figure 10) and triplet yield (Table II) with the 1-alcohol which are not very different from those of 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 fluorescence spectra. Compared to the fluorescence spectrum of 1-methylnaphthalene, the fluorescence spectra of our compounds show diminished intensity in the region of the $n \rightarrow \pi^*$ absorption band of the benzophenone groups. This observation is most easily seen in the spectrum of 2.

One may follow in detail the paths of excitation transfer in compounds 1, 2, and 3 (Figure 1). *In these 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 over-all effect of the transfer is an enhancement of the yield of the naphthalene group triplets.

The fluorescence decay rate for 1-methylnaphthalene is about 10^7 sec.$^{-1}$.[36] Therefore, not only is the efficiency of singlet transfer (about 75% in 2, 85% in 3, and 90% in 1) less efficient than triplet transfer (100%

in all cases), but *the rate of singlet energy transfer ($k \sim 10^7$–10^8 sec.$^{-1}$)[37] is much slower than the rate of triplet excitation transfer ($k > 10^{10}$ sec.$^{-1}$)!*

A calculation using the Förster relationship[4b] 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 have expected totally efficient intramolecular singlet excitation transfer by this mechanism in the compounds because of the dependence of transfer rate on r^{-6}. Furthermore, at such close approach of the donor and acceptor, higher multipole interactions could also contribute to the transfer probability. One might have expected that exchange interactions due to overlap of chromophore electron clouds, which might be the favored means for the triplet excitation transfer, would also operate efficiently for singlet excitation transfer.[38] However, transfer by any mechanism cannot account for the distortion of the donor emission spectrum. As already mentioned, the fluorescence spectra of the 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 2 can be fairly closely matched by "subtracting" the long wave length absorption band of 4-methylbenzophenone from the fluorescence spectrum of 1-methylnaphthalene. This is not the case for 1 and 3. The fluorescence spectra of 1 and 3 also show diminished intensity in the region (>3900 Å.) where 4-methylbenzophenone does not absorb. Thus there are *at least two singlet excitation transfer mechanisms operating,* including one that has, at least that characteristic of the trivial process, namely distortion of the donor–emission spectrum. In the case of 2, the latter mechanism dominates. Finally, it is mentioned again that at the sample size and concentration (10^{-3} M) employed for the fluorescence measurements little, if any, intermolecular excitation transfer takes place. At any rate, the fluorescence spectrum of 1-methylnaphthalene is hardly affected by the presence of 4-methylbenzophenone (10^{-3} M) in the solution (Figure 4).

Finally, the nature of the singlet excitation transfer mechanism that leads to distortion of the donor-emission spectrum in our compounds is not understood at this time. It is difficult to conceive of genuine emission–reabsorption operating at such close approach of donor and acceptor and equally difficult to conceive of another mechanism that leads to the observed distortion of the naphthalene group fluorescence spectrum. The synthesis of stiff molecules containing naphthalene and benzophenone moieties at various distances apart is in progress. If the relative orientation of the two chromophores can be determined in some of these compounds, more detailed information about the intramolecular excitation transfer processes would ensue.

(34) It must be kept in mind that only about 10% of the naphthalene triplets undergo radiative decay, while nonradiative decay $S_1 \rightarrow S_0$ decay in naphthalene at 77°K. is probably not very important.[35]

(35) At the concentration used in the triplet-counting experiments (0.01 M), intermolecular transfer of singlet excitation *via* the trivial process could be important. However, the fluorescence spectra of the compounds recorded at lower concentration (0.001 M) exhibit very 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.

(36) S. G. Hadley, H. E. Rast, and R. A. Keller, *J. Chem. Phys.*, **39**, 705 (1963).

(37) It is assumed that rate of fluorescence and the rates of other radiationless deactivation processes for the naphthalene moieties in our compounds are not very different from those for 1-methylnaphthalene.

(38) It is conceivable that the exchange interaction is larger in the case of triplet excitation transfer since triplet-state wave functions might be more extensive than singlet-state wave functions so that greater overlap could result in the triplet case.

# Proton Affinities and the Methyl Inductive Effect[1]

M. S. B. Munson

Contribution from the Humble Oil and Refining Company, Research and Development, Baytown, Texas. Received December 22, 1964

The relative proton affinities or basicities of some polar hydrocarbon derivatives have been measured in the gas phase by observation in the source of a mass spectrometer of very rapid proton-transfer reactions from a protonated molecule to a neutral molecule of a different species. For the molecules studied, replacement of hydrogen by a methyl group increased the base strength of the molecule. Agreement between relative proton affinities from proton-transfer reaction and gas phase ion energetics is good. It was determined that $P(H_2O) < P(CH_3OH) < P(CH_3OCH_3)$; $P(HCHO) < P(CH_3CHO) < P(CH_3COCH_3)$; $P(CHOOH) < P(CH_3COOH)$; $P(NH_3) < P(CH_3NH_2) < P[(CH_3)_2NH] < P[(CH_3)_3N]$.

Introduction

The relative acidities or basicities of a series of compounds can be determined readily in solution in a given solvent. However, theoretical predictions about variations in acidity or basicity with molecular structure are based on properties of isolated molecules. The observed variations in solution are the result of changes in solvation effects on molecular and ionic species as well as changes in acidity or basicity of the molecules. Separation of these two effects is virtually impossible, so that interpretation of differences in dissociation constants in terms of molecular models must be done with extreme caution.[2] Determination of the acidities or basicities of different solvents is even more complicated, and discussions of these differences in terms of molecular properties is fraught with pitfalls.[2a] The basicities determined from solution studies are directly related to practical chemistry but, because of the unknown nature of the reactants, are virtually impossible to interpret. A determination of the base strengths of a series of molecules with a known acid under conditions which will give theoretically meaningful results would be valuable.

It is possible to determine directly in some cases the proton affinities of molecules in the gas phase

$$B + H^+ \longrightarrow BH^+ \qquad P(B) \equiv -\Delta H_r \qquad (1)$$
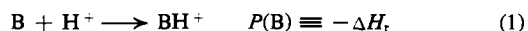
where the proton affinity, $P(B) = -[\Delta H_f(BH^+) -$

$\Delta H_f(H^+) - \Delta H_f(B)]$. The proton affinity is, therefore, a direct measure of the Brønsted base strength of the molecule. Proton affinities can be determined in several ways. The proton affinity of NH_3 can be obtained from thermodynamic cycles of crystalline ammonium salts and $P(H_2O)$ has been estimated from an analogy to this process.[3]

Several protonated species, H_3O^+, $CH_3OH_2^+$, $RCOOH_2^+$, are formed as rearrangement ions in the mass spectra of many compounds so that it is possible to determine the heats of formation of some of these ions and, therefore, the proton affinities of the neutral molecules.[4]

It is generally considered that ionic reactions observed in mass spectrometric studies have essentially no activation energy and that the reactions which occur are, therefore, thermoneutral or exothermic.[5,6] This criterion may be used to set an upper limit on heats of formation of ions and hence a lower limit for the proton affinities when the energies of the other species are known. Tal'roze and Frankevich suggested that reactions unobservable in the mass spectrometer could be considered as endothermic, and they calculated an upper limit for proton affinities of H_2O, CH_3OH, and C_2H_5OH as well.[7,8] This second criterion can be readily demonstrated as false in many cases,[9,10] but it is perhaps valid for the proton-transfer reactions which they were considering.

Recently, work has been done in these laboratories on ionic reactions in a mass spectrometer at pressures up to several tenths of a torr and it has been possible to observe reactions of secondary and even higher-order product ions at the highest pressures attainable.[11] At high pressures in the mass spectrometer source it is possible to make direct observation of proton-transfer reactions of several simple protonated organic compounds and therefore to determine the order of basicity

(1) Supported in part by Project Squid under Contract Nonr-3623 (S-18).

(2) (a) For an excellent discussion on these topics, see R. P. Bell, "The Proton in Chemistry," Cornell University Press, New York, N. Y., 1959; (b) E. M. Arnett, "Progress in Physical Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, pp. 223-403.

(3) J. Sherman, *Chem. Rev.*, 11, 164 (1932).

(4) (a) D. Van Raalte and A. G. Harrison, *Can. J. Chem.*, 41, 3118 (1963); (b) M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, 68, 3191 (1964).

(5) F. W. Lampe, J. L. Franklin, and F. H. Field, "Progress in Reaction Kinetics," Vol. I, Pergamon Press, Oxford, 1961.

(6) V. L. Tal'roze, *Pure Appl. Chem.*, 5, 455 (1962).

(7) V. L. Tal'roze and E. L. Frankevich, *Dokl. Akad. Nauk SSSR*, 111, 376 (1956).

(8) E. L. Frankevich and V. L. Tal'roze, *Zh. Fiz. Khim.*, 33, 1093 (1959).

(9) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, 68, 3098 (1964).

(10) J. L. Franklin and M. S. B. Munson, 10th International Combustion Symposium, Cambridge, England, 1964.

(11) F. H. Field, *J. Am. Chem. Soc.*, 83, 1523 (1961).