Intramolecular Energy Transfer between Triplet States of Weakly Interacting Chromophores. III. Compounds in Which the Chromophores Are Separated by a Rigid Steroid Bridge

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Abstract: The intramolecular transfer of triplet excitation between chromophores held approximately 15 Å apart by a rigid steroid bridge was measured for two molecules. The acceptor in both cases is the naphthalene chromophore. In I the donor is the benzophenone chromophore and in II the donor is the carbazole chromophore. The rate constant for transfer is 25 $\sec^{-1}$ for I and 0.04 $\sec^{-1}$ for II. The 1000-fold difference in these rate constants is paralleled by the 1000-fold difference in the triplet-state lifetime for the two donor chromophores. In both cases the transfer of singlet excitation energy was more complete than the transfer of triplet excitation energy.

Recently several workers have studied the intramolecular transfer of triplet excitation energy between two relatively isolated chromophores on the same molecule.[2] The goal of these studies was to gain some insight into the mechanism of triplet excitation energy transfer. Intermolecular transfer of triplet excitation is known to occur and has been well studied.[3-8] Unfortunately, studies of intermolecular triplet excitation transfer must be conducted in highly concentrated (0.1 *M*) rigid glass solutions at 77°K. At these concentrations and temperatures it is impossible to eliminate complex formation or small crystallites as contributing to the mechanism for energy transfer. Previous studies of intramolecular energy transfer have contributed little to the understanding of the mechanisms involved for two principal reasons. (1) The transfer of the triplet excitation energy from the donor to the acceptor was essentially complete within experimental error. This prevented an estimation of the rate of transfer because it was too large. (2) Some of the compounds were not structurally rigid, and there was a possibility that the molecules could twist around and form an intramolecular complex.

Both of the above difficulties were eliminated in the present work.[9] A *rigid*, saturated, steroid bridge was used to increase the separation between the chromophores and hence decrease the rate of transfer and eliminate the possibility of intramolecular complex formation. The distance between the chromophores was determined by measuring the amount of singlet energy transferred between the chromophores and using the results in conjunction with the formulas developed by Förster, and tested by others,[10-12] to calculate the distance. This distance agreed well with distances estimated from measurements on molecular models. Both the rate of energy transfer and the distance between the chromophores was determined for the molecules discussed below.

The measurements of fluorescence and phosphorescence were made in a rigid-glass matrix at 77°K. This rigid matrix does not permit molecular rotation or diffusion and eliminates transfer mechanisms involving internal vibrational molecular motions which bring the two chromophores close together during the lifetime of the excited state. Intermolecular mechanisms were eliminated by studying model solutions of mixtures of the two separated chromophores.

Molecules Studied

The energy-transfer properties of I and II in Figure 1 are the subject of this work. Molecules III, IV, and V were used as model compounds to study the spectral properties of the separated chromophores. The stereochemistry of I and II is somewhat in doubt, but the behavior of these compounds on crystallization indicates that only one epimer is predominately present. The synthesis and purification of these compounds is discussed in the Experimental Section.

The triplet donors in I and II are the ester of benzophenone-4-carboxylic acid (I) and the carbazole chromophore (II). The triplet acceptor in both cases is the naphthalene chromophore.

The singlet energy levels of I and II are such that it is

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[2] (a) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2670 (1963); **87**, 2322 (1965); (b) D. E. Breen and R. A. Keller, *ibid.*, **90**, 1935 (1968); R. A. Keller, *ibid.*, **90**, 1940 (1968).

[3] V. L. Ermolaev, *Soviet Phys.-Usp.*, **80**, 333 (1963), and references therein.

[4] B. Smaller, E. C. Avery, and J. R. Remko, *J. Chem. Phys.*, **43**, 922 (1965).

[5] J. B. Farmer, G. L. Gardner, and C. A. McDowell, *ibid.*, **34**, 1058 (1961).

[6] S. Siegel and L. Goldstein, *ibid.*, **43**, 4185 (1965).

[7] J. K. Roy and M. A. El-Sayed, *ibid.*, **40**, 3442 (1964).

[8] M. Inokuti and F. Hirayama, *ibid.*, **43**, 1978 (1965).

[9] A preliminary report of this work has been published; see R. A Keller and L. Dolby, *J. Am. Chem. Soc.*, **89**, 2768 (1967).

[10] Th. Förster, *Discussions Faraday Soc.*, **27**, 7 (1959).

[11] S. A. Latt, H. T. Cheung, and E. R. Blout, *J. Am. Chem. Soc.*, **87**, 995 (1965).

[12] L. Stryer and R. Haugland, *Proc. Natl. Acad. Sci. U. S.*, **58**, 719 (1967).

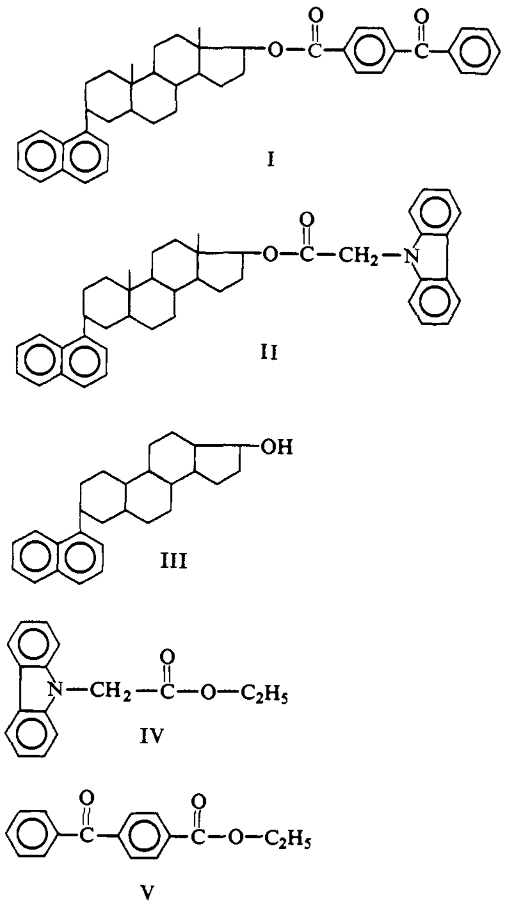


Figure 1. Structure of the molecules studied.

possible to excite the triplet donor chromophores in both cases with long-wavelength radiation which is not absorbed by the naphthalene chromophore.

The purity of the samples was checked by thin layer chromatography. Compound I showed only one spot, but compound II showed one predominant spot and three weak impurity spots. The spot corresponding to pure compound II was scraped off of the backing and the material eluted from the silica gel. All measurements, with the exception of the absorption spectrum, were made with this 0.03 mg[13] of material.

Absorption Spectra

The absorption spectra discussed in this section were measured on a Cary 12 spectrophotometer. The solvent was Spectrograde cyclohexane. All absorption measurements were made at room temperature.

The spectra of I and II and their separated parts are displayed in Figures 2 and 3. In both cases the sum of the extinction coefficients of the moieties is equal to the spectrum of the compound molecule. Note that in both cases it is easy to excite the triplet donor chromophore with long-wavelength radiation which is not abosrbed by the naphthalene chromophore.

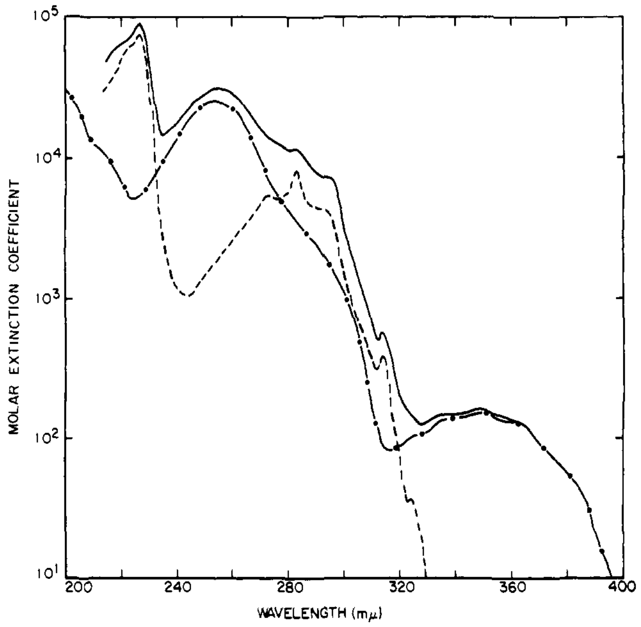
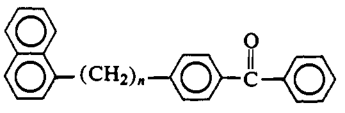


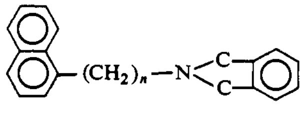
Figure 2. Absorption spectra: ———, I; — — —, III; — · —, V.

Lamola, Leermakers, Byers, and Hammond[2a] studied compounds of the formula



n = 1, 2, and 3

Breen and Keller[2b] studied compounds of the formula



n = 0, 1, 2, and 3

Both groups of workers observed absorption and emission in these compounds which was not characteristic of either chromophore. Breen and Keller tentatively identified this absorption and emission as being charge transfer in nature.[2b] No absorption or emission which was not characteristic of either chromophore was observed in the molecules studied in this paper.

Fluorescence Spectra

Fluorescence spectra were excited with an ac, 200-W, high-pressure, Hg lamp. The 120-cycle radiation from this lamp was passed through a large-aperture monochromator and onto the sample. The fluorescence emission, at right angles to the excitation light, was then passed into a 0.5-m Ebert scanning monochromator. The exit radiation was detected with a 1P28 photomultiplier tube and the resulting signal amplified with a phase-sensitive amplifier. The output signal was displayed on a strip chart recorder. The reference signal for the phase-sensitive detector was derived from an unfiltered full-wave rectifier attached to the same ac line as

[13] Identification and estimation of the amount was made by measuring the relative absorption spectrum.

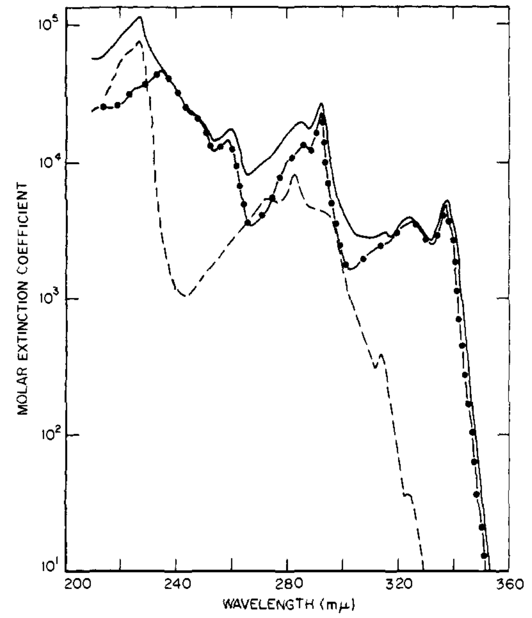


Figure 3. Absorption spectra: ———, II; — — —, III; — • —, IV.

the excitation lamp. No attempt was made to correct the spectral intensities for variations in the response of the detector and monochromator with wavelength. The excitation wavelength was 299 nm with a half-width of 5 nm at the most. Samples were contained in Vycor tubes of approximately 5-mm i.d. All fluorescence measurements were made at 77°K in a rigid matrix composed of 30% butyl alcohol and 70% isopentane.[14] Concentrations of solute were 10^{-5} *M*.

The fluorescence spectra of I and mixtures of I and III are shown in Figure 4. The benzylbenzoate (V) chromophore has the lowest energy excited state in I and acts as a singlet excitation energy acceptor for singlet energy transferred from the naphthalene chromophore.[15] The lowest singlet excited state of benzoylbenzoate is of n-π* character and does not fluoresce. The fluorescence from I shown in part A is from the naphthalene chromophore and is the result of incomplete transfer of excitation away from the naphthalene chromophore. The fluorescence shown in part B gives an indication of what the emission of I would look like if no energy transfer were occurring. A careful comparison of part A and part C in Figure 4 shows that ~70% of singlet excitation energy is being transferred away from the naphthalene chromophore in I. This point will be discussed in more detail below.

The fluorescence spectra of II and mixtures of II and III are shown in Figure 5. In this case the carbazole chromophore, which is the singlet excitation energy acceptor, fluoresces. The fluorescence of the carbazole chromophore is shown in part A of Figure 5. Part B shows a combination of naphthalene and carbazole fluorescence from a mixture of II and III. A careful comparison of part A and part C in Figure 5 shows that ~90–95% of the singlet excitation energy is being transferred away from the naphthalene chromophore in II. Again, this point will be discussed in more detail below.

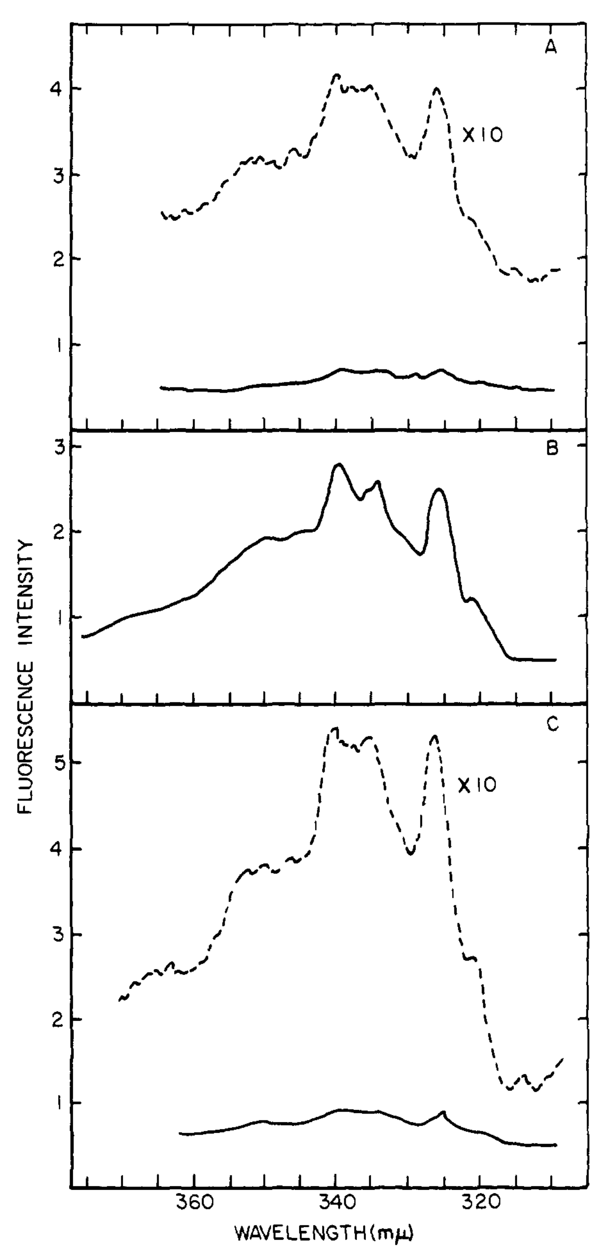


Figure 4. Fluorescence emission spectra: A, I (5.2 × 10^{-6} *m*); B, I (5.2 × 10^{-6} *m*) + III (1.5 × 10^{-5} *m*); C, I (5.2 × 10^{-6} *m*) + III (1.5 × 10^{-6} *m*).

It is possible to use formulas developed by Förster[10] to correlate the amount of singlet energy transferred from a donor to an acceptor chromophore with the distance between the chromphores. The data given above were used to calculate the distances between the chromophores in I and II, and the results are listed in Table I. More details of this calculation are given in the Appendix.

Phosphorescence Spectra

Phosphorescence spectra were excited with a high-pressure, dc, 500-W, Hg–Xe lamp. The excitation light was isolated from the spectrophotometer by means of a rotating shutter phosphoroscope. Two shutter speeds, 20 and 400 Hz, were used. The time resolution between excitation and observation at the fast shutter speed is 1.2 msec. A 0.5-m Ebert scanning monochromator was placed at 180° from the excitation lamp. Radiation

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(14) The butyl alcohol and isopentane were fluorescence-free solvents.

(15) It is somewhat confusing that the *triplet donor* chromophore in I and II is also the *singlet acceptor*.

Table I

Measurement	Result: Compound I	Result: Compound II
Absorption spectrum	Extinction coefficient is sum of extinction coefficients of separated chromophores	Extinction coefficient is sum of extinction coefficients of separated chromophores
Comparison of fluorescence intensity of compound with that of model singlet donor	70% of singlet excitation energy is transferred	95% of singlet excitation energy is transferred
Distance between chromophores calculated from above results using Förster's theory	14 Å	15 Å
Distance between chromophores measured from molecular models	~15 Å	~15 Å
Comparison of phosphorescence intensity of compound with that of model triplet donor	35% of triplet excitation energy transferred	. . .[a]
Comparison of phosphorescence intensity from triplet-donor chromophore and triplet-acceptor chromophore	39% of triplet excitation energy transferred	30% of triplet excitation energy transferred
Comparison of phosphorescence lifetime of compound with that of model triplet donor	12% of triplet excitation energy transferred. Rate constant for transfer process is 25 sec^{-1}	21% of triplet excitation energy transferred. Rate constant for transfer process is 0.04 sec^{-1}

[a] Measurement could not be made because of experimental difficulties.

leaving the monochromator was detected with a 1P21 photomultiplier tube. The signal from the photomultiplier was passed through an RC circuit with a 1-sec time constant and into a high input impedance, strip chart recorder. All phosphorescence spectra were observed at 77°K in the rigid matrix described above.

The phosphorescence spectra of I and a mixture of V and naphthalene are shown in Figure 6A. The excitation radiation was filtered[16] to remove visible light. The spectrum of I shows some naphthalene emission in the presence of the strong phosphorescence characteristic of the triplet donor, but no naphthalene emission is visible from the mixture of V and naphthalene. This is strong evidence that triplet excitation energy transfer occurs in I. Careful measurement of the ratio of the phosphorescence intensities from I and V shows that approximately 65% of the triplet excitation energy is not transferred in I.

A slowly rotating phosphoroscope was used to eliminate the intense emission from the triplet donor in I and permit the observation of the emission from the naphthalene chromophore. This spectrum is shown in Figure 6B. The triplet-acceptor emission from I is almost identical with the naphthalene phosphorescence from III. The naphthalene phosphorescence from I was excited through a Corning O-52 filter which did not transmit radiation which could directly excite the naphthalene chromophore.[17] This means that the excitation of the naphthalene chromophore must be *via* the triplet-donor chromophore. A photomultiplier tube and oscilloscope were used to measure the ratio of the *total* emission of the fast component (benzophenone chromophore) to the slow component (naphthalene) of the phosphorescence. The result was that $I(\text{slow})/I(\text{fast}) = 0.25/4.0$.[18] The phosphorescence quantum yield of V is approximately ten times greater than that of naphthalene.[19] Using this number and the above result for the ratio of the intensities, it is easy to show that approximately 40% of the excitation energy is transferred from the triplet donor to the triplet acceptor in I.

The phosphorescence spectra of II and a mixture of IV and naphthalene are shown in Figure 7. Again, emission from the naphthalene chromophore is visible from II but not from the mixture. Corning 7-54 and O-54 filters were used in the excitation beam to prevent direct excitation of the naphthalene chromophore; hence emission from the naphthalene chromophore in II is indicative of energy transfer. Unfortunately, the phosphorescence lifetimes of naphthalene and carbazole are too similar to use time resolution as a method of measuring the amount of emission from each chromophore in II. If it is assumed that the peak height at 447 nm is characteristic of the naphthalene phosphorescence in the same way that the peak height at 440 nm is characteristic of the carbazole phosphorescence, the intensity of emission from each chromophore can be estimated from Figure 7. If the phosphorescence quantum yield of naphthalene is equal to the phosphorescence quantum yield of carbazole,[20] the graph in Figure 7 indicates that about 30% of the triplet excitation energy is transferred from the carbazole chromophore to the naphthalene chromophore.

Lifetime Measurements

Lifetimes were measured by photographing oscilloscope displays of the phosphorescence decays. The time base of the oscilloscope was calibrated with a time-mark generator. A fast (3-μsec half-width) xenon flash lamp was used to excite compounds with lifetimes in the millisecond region. The photomultiplier was protected from the excitation flash by using complementary filters and a well-collimated detection path at 90° from the excitation path.

Logarithmic plots of the phosphorescence decays of I and V are shown in Figure 8.[21] The phosphorescence

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[16] Corning 7-54 + 2.5 cm of a solution of 90 g of $CoSO_4 \cdot 7H_2O$ and 500 g of $NiSO_4 \cdot 6H_2O$ in a liter of water.

[17] No naphthalene emission was visible from III when this filter was placed in the excitation beam.

[18] No corrections were made for the change in sensitivity of the apparatus as a function of wavelength.

[19] φ_p for benzophenone is approximately 1 while φ_p for naphthalene is approximately 0.1.

[20] This is not a bad assumption. The quantum yields are certainly of the same order of magnitude. Answers from this type of reasoning are only qualitative.

[21] The deviation of the decay of V from a simple logarithmic form is probably due to a small amount of impurity. This impurity was not removed by zone refining.

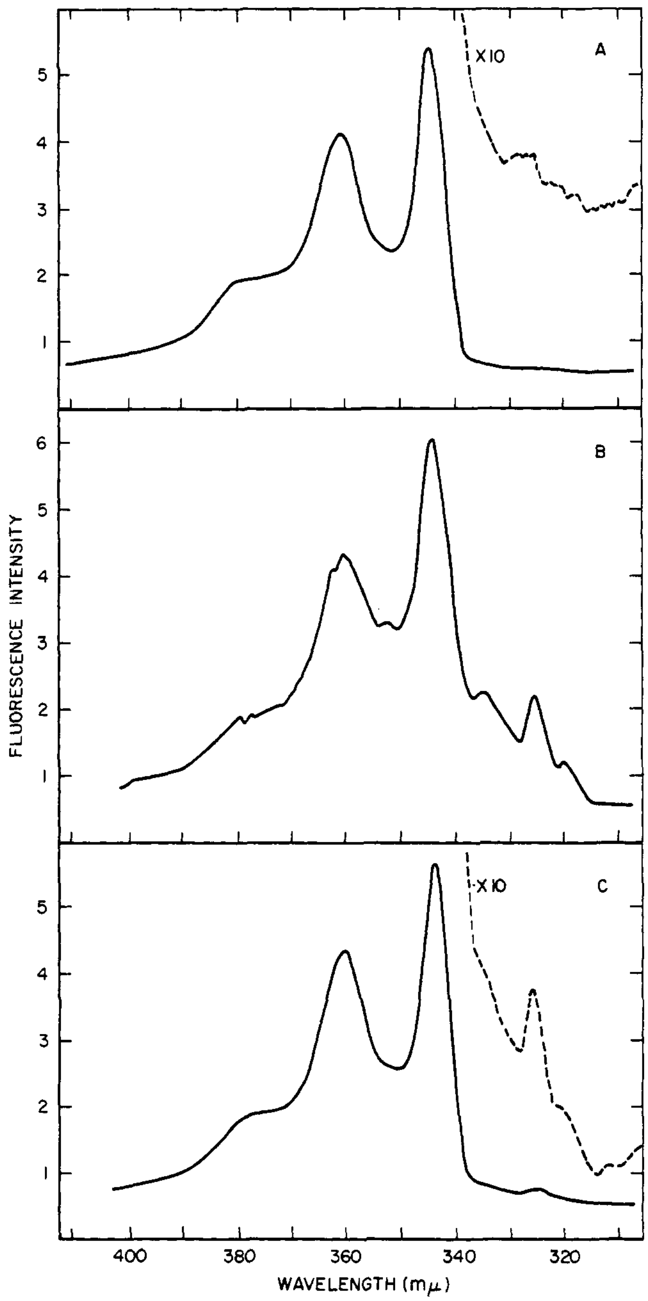

Figure 5. Fluorescence emission spectra: A, II (5.7×10^{-6} *m*); B, II (5.7×10^{-6} *m*) + III (1.5×10^{-5} *m*); C, II (5.7×10^{-6} *m*) + III (1.5×10^{-6} *m*).

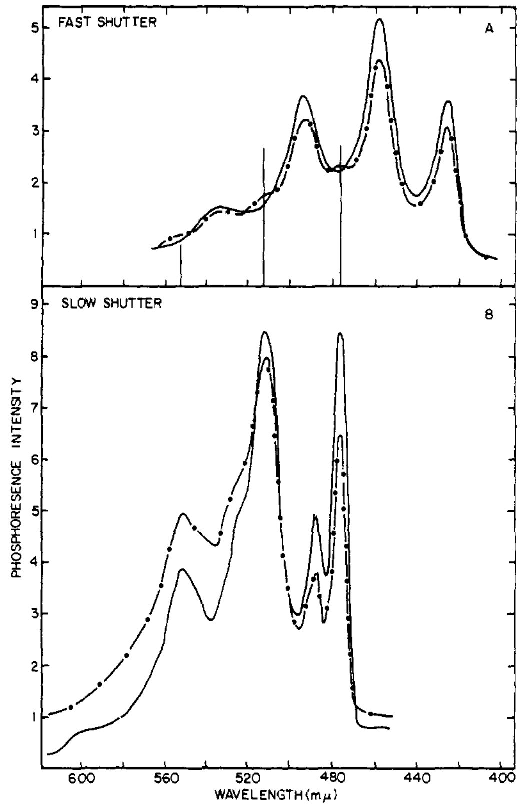

Figure 6. Phosphorescence emission spectra: A, — · —, I; ———, V + naphthalene (all concentrations were 1.6×10^{-4} *m*); B, ———, I; — · —, III.

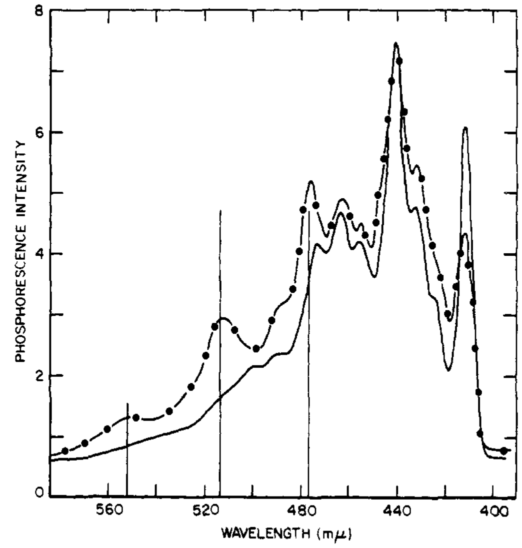

Figure 7. Phosphorescence emission spectra: — · —, II; ———, IV + naphthalene (all concentrations were 3×10^{-4} *m*).

decay of I is appreciably faster than the phosphorescence decay of V. This is presumably due to the addition of a triplet excitation energy-transfer process which is also first order. The difference in lifetime between I and V is larger than would be expected by chemical substitutions of the ester group. The difference between the first-order rate constants (reciprocal lifetimes) indicates that 12% of the energy is transferred away from the benzophenone chromophore and that the rate constant for the transfer process is 25 $\sec^{-1}$.

Logarithmic plots of the phosphorescence decays of II and IV are shown in Figure 9. Again the appreciable difference in the lifetimes indicates energy transfer in II. The difference between the first-order rate constants shows that 21% of the triplet excitation energy is transferred away from the carbazole chromophore and that the rate constant for the transfer process is about 0.04 $\sec^{-1}$.

Summary of Experimental Results

The most important result of this work is that the transfer of triplet excitation energy in these compounds is relatively inefficient and *less* than the transfer of singlet excitation energy.

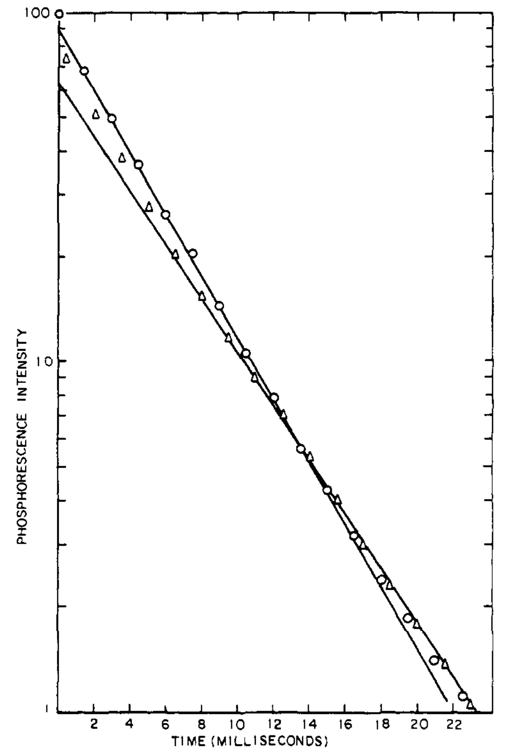

Figure 8. Phosphorescence decay measurements: ○, I; △, V.

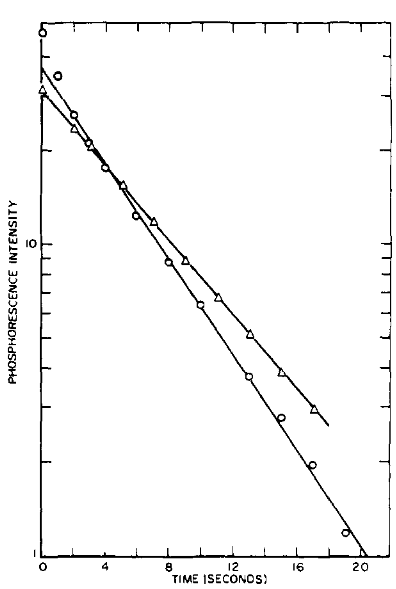

Figure 9. Phosphorescence decay measurements: ○, II; △, IV.

The quantitative interpretation of the numbers obtained is open to some question because of the nature of the measurements and the approximations and assumptions which must be made. However, some confidence can be placed in the conclusions when several independent sets of measurements and assumptions lead to the same results. The quantitative results of the measurements discussed in the experimental section are displayed in Table I. It is seen that the agreement among the several methods is good.

Discussion

The most important conclusion of this work is that the transfer of triplet excitation energy is a relatively short-ranged process. In both cases the transfer of singlet excitation energy was more complete than the transfer of triplet excitation energy.

The fact that the rate of transfer of triplet excitation energy is 600 times larger in I than it is in II is somewhat surprising. It is generally assumed that the predominant coupling between the triplet states of the two moities arises from electron-exchange integrals between the wave functions of the two chromophores.[22-24] The distances between the chromophores in I and II are similar, and it might be expected that the exchange integrals would be similar. Another mechanism for the exchange of excitation energy involves the coupling of the transition dipoles of the two chromophores. When this mechanism is dominant the transfer rate depends upon the magnitude of the transition dipole of both the donor and acceptor. An approximation of the ratio of the transition dipoles of the triplet donors in I and II can be obtained from the phosphorescence lifetimes of these chromophores. The phosphorescence lifetime of IV is 7 sec and of V is 6×10^{-3} sec. The ratio of the lifetimes is approximately 1000 and is in good agreement with the ratio of the transfer rates. This suggests that a dipole–dipole coupling mechanism may be responsible for the transfer of triplet excitation energy in these compounds. However, there are two strong points against a normal dipole–dipole coupling mechanism.[3] (1) When numbers are put into the standard equations[10] to estimate the transfer distance, it is found that, when the transition vector of the acceptor involves a forbidden singlet → triplet transition, the transfer distance can be no more than 2 or 3 Å. (2) The transfer probability for triplet energy transfer was found to be independent of the oscillator strength of the S → T transition in the acceptor.[3] A possible explanation of the dilemma discussed above is that the rigid bridge between the chromophores (and or the solvent) participates in the energy-transfer process by a mechanism proposed by McConnell,[25] and discussed by Robinson, and Frosch,[26] which involves virtual states of the "host" as intermediates in the energy-transfer process. If the leading term in the interaction of the donor chromophore and the first host state is dipole–dipole in character, then the rate of transfer would depend upon the strength of the transition vector to this state.

It must be emphasized that differences in the structure (the presence of an acyl oxygen in I) and wave functions of I and II may lead to sufficient differences in the exchange integrals in these two molecules to explain the differences in the transfer rate. In this case the argument favoring a dipole–dipole coupling mechanism would not apply, and it is just a coincidence that the ratio of the transfer rates is similar to the ratio of the triplet lifetimes.

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(22) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

(23) D. M. Hanson and G. W. Robinson, *ibid.*, **43**, 4174 (1965); G. W. Robinson and R. P. Frosch, *ibid.*, **37**, 1962; **38**, 1187 (1963); G. C. Nieman and G. W. Robinson, *ibid.*, **39**, 1298 (1963).

(24) W. Jortner, S. A. Rice, J. L. Katz, and S. I. Choi, *ibid.*, **42**, 309 (1965).

(25) H. M. McConnell, *ibid.*, **35**, 508 (1961).

(26) G. W. Robinson and R. P. Frosch, *ibid.*, **38**, 1187 (1963).

Experimental Section

3-Naphthyl-5α-androstan-3,17β-diol. To the Grignard reagent prepared from 14.9 g of α-bromonaphthalene and 2.30 g of magnesium in tetrahydrofuran solution was added 5.974 g of 5α-androstan-17β-ol-3-one in the tetrahydrofuran. The resulting mixture was refluxed overnight and processed in the usual manner to yield 2.1 g (25%) of the diol, mp 200–204°, after two crystallizations from ethyl acetate–methanol. Additional diol could be obtained by chromatographing the mother liquors.

3-Naphthyl-5α-androst-2- or -3-en-17β-acetate. A solution of 380 mg of 3-naphthyl-5α-androstan-3,17β-diol in 10 ml of acetic anhydride was treated with 4 drops of acetyl chloride and heated under reflux for 1 hr. The reaction mixture was poured over ice and 10 g of sodium carbonate. The resulting mixture was extracted with ether to afford the unsaturated acetate. Crystallization from ether–hexane afforded 200 mg (49%) of material, mp 157–158°.

3-Naphthyl-5α-androstan-17β-acetate. A solution of 453 mg of the unsaturated acetate obtained above in ethyl acetate was hydrogenated over 100 mg of 10% palladium on carbon. The theoretical amount of hydrogen was consumed in 24 hr, and the crude product was isolated in the usual manner and crystallized from acetone to afford 200 mg (44%) of material, mp 127–128°.

3-Naphthyl-5α-androstan-17β-ol. A solution of 200 mg of the acetate in 30 ml of ethanol was treated with 0.4 g of sodium hydroxide and heated under reflux overnight. The reaction mixture was processed in the normal manner and the crude alcohol was crystallized from acetone to afford 150 mg (82%) of material, mp 141–142°. *Anal.* Calcd for $C_{29}H_{38}O$ (402.62): C, 86.5; H, 9.5. Found: C, 86.5; H, 9.5.

3-Naphthyl-5α-androstane-17β-(*p*-benzoylbenzoate). *p*-Benzoylbenzoyl chloride was prepared by refluxing 300 mg of *p*-benzoylbenzoic acid with 10 ml of thionyl chloride for 1 hr after which the thionyl chloride was evaporated under reduced pressure. The residue was taken up in 20 ml of benzene and evaporated under reduced pressure, a procedure which was repeated three times. The *p*-benzoylbenzoyl chloride was added to a solution of 150 mg of 3-naphthyl-5α-androstan-17β-ol in 15 ml of benzene, and 1 ml of pyridine was added. The reaction mixture was stirred for 4 hr after which the ester was isolated in the usual manner and filtered through a Florosil column with benzene. The crude ester was crystallized from chloroform–hexane to yield 65 mg (28%) of material, mp 187–188°. *Anal.* Calcd for $C_{43}H_{46}O_3$ (610.85): C, 84.5; H, 7.6. Found: C, 84.8; H, 7.6.

3-Naphthyl-5α-androstan-17β-(9-carbazoleacetate). A solution of 50 mg of 3-naphthyl-5α-androstan-17β-ol and 100 mg of 9-carbazoleacetic acid in 20 ml of dry toluene containing a crystal of *p*-toluenesulfonic acid was heated under a water separator. After 8 hr the cooled reaction mixture was washed with sodium carbonate solution and then water. The crude product was filtered through a Florosil column and crystallized from cyclohexane to afford 25 mg (32%) of material, mp 193.5–194.5°. *Anal.* Calcd for $C_{43}H_{47}O_2N$ (609.8): C, 84.7; H, 7.8; N, 2.3. Found: C, 84.2; H, 7.7; N, 2.3.

Appendix

Use of Singlet Energy Transfer to Estimate the Distance between the Chromophores. The theory of energy transfer by a dipole–dipole coupling mechanism was developed by Förster.[10] The expressions which relate the transfer probability to the distance between the chromophores are given below.

$$T = \frac{(R_0/R)^6}{1 + (R_0/R)^6}$$

T is the transfer probability, *R* is the distance between the chromophores, and R_0 is given by the following expression.[27,28]

$$R_0^{\,6} = \frac{9000 \ln 10 \beta^2 \varphi_f}{128\pi^5 n^4 N} J$$

β is an orientation factor which depends upon the angle between the dipoles, φ_f is the fluorescent quantum yield of the donor, *n* is the refractive index of the solution, *N* is Avogadro's number, and *J* is a spectral overlap integral defined below.

$$J = \int_0^\infty I(\lambda)\varepsilon(\lambda)\lambda^4 \, d\lambda$$

$I(\lambda)$ is the emission spectrum of the donor normalized to the condition that

$$\int_0^\infty I(\lambda) d\lambda = 1$$

$\varepsilon(\lambda)$ is the extinction coefficient of the acceptor.

The orientation of the transition dipoles was not known and a value of 0.5 was assumed for β^2.[27] This is the value which results from a random distribution of the orientation of the transition vectors. The refractive index of the glassy solvent at 77°K is 1.52.[29] The absorption and emission properties of the model compounds were used to calculate *J*. The fluorescence spectrum was not corrected for the change in instrument sensitivity as a function of wavelength. This does not introduce a large error because *R* depends upon the sixth root of *J* and β^2.

A summary of the results of the calculation is given in Table II.

Table II

Molecule	*J*, 10^{-3} cm^6/mole	R_0, Å	*T*	*R*, Å
I	3.4×10^{-16}	16.3	0.70	14
II	4.2×10^{-15}	24.8	0.95	15

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(27) M. Z. Maksimov and I. M. Rozman, *Opt. Spectry.* (USSR), **12,** 337 (1962).

(28) The corrected Forster equation is given in ref 11.

(29) H. E. Rast, Ph.D. Thesis, University of Orgeon, 1964.