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Intramolecular Energy Transfer between Triplet States of Weakly Interacting Chromophores. I. Compounds in Which the Chromophores are Separated by a Series of Methylene Groups[1a,b]

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Contribution from the National Bureau of Standards, Washington, D. C. 20234, and the Department of Chemistry, University of Oregon, Eugene, Oregon.
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Abstract: The intramolecular transfer of triplet excitation energy from the donor chromophore (phthalimide and carbazole) to the acceptor chromophore (naphthalene) was studied when the chromophores were separated by methylene groups. In all cases, complete transfer of triplet excitation energy occurred. In some cases absorption and emission bands not characteristic of either chromophore were observed and were attributed to an excited electronic state involving charge transfer from the naphthalene chromophore to the phthalimide chromophore.

The transfer of triplet excitation energy between two isolated chromophores on the same molecule was studied for the compounds shown in Figure 1. In many respects the results of this work amplify and confirm the results obtained by Hammond, *et al.*, who studied a similar series of molecules.[2] The most important conclusion of both their work and ours is that in all cases the only phosphorescence observed was characteristic of the chromophore which had the lowest triplet excitation energy. This was true even when the initial excitation was localized on the chromophore with the highest triplet excitation energy. In addition we have attributed the anomalous absorption and emission bands observed by them and by us to involve an excited electronic state in which electronic charge has been transferred from the naphthalene chromophore to the phthalimide chromophore.

In part II of this series[3a] the energy-transfer properties of two chromophores held at right angles to each other by a spiro linkage are discussed. Part III is concerned with the effect of separating the two chromophores by a rigid steroid bridge.[3b]

The intermolecular transfer of triplet excitation energy in rigid-glass solutions has been studied by several workers.[4-9] The results of these works are interpreted to indicate that triplet excitation energy can be transferred between chromophores which are separated by 10–15 Å. In practice, the interactions are so weak that it is necessary to employ concentrations of the donor and acceptor in the range of 10^{-2} to 10^{-1} *M* in order to detect transfer. At these concentrations it is quite possible that the distribution of molecules in the

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[1] (a) This research was supported by the Advanced Research Projects Agency; (b) based in part upon a dissertation submitted by D. E. Breen to the Graduate School, University of Oregon, in partial fulfillment for the degree of Master of Science, 1965; (c) Philco-Ford Corp., Aeronutronic Division, Newport Beach, Calif. 92663.

[2] A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2670 (1963); 87, 2322 (1965).

[3] (a) R. A. Keller, *ibid.*, 90, 1940 (1968); (b) a preliminary report of this work has been published; see R. A. Keller and L. Dolby, *ibid.*, **89**, 2768 (1967).

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

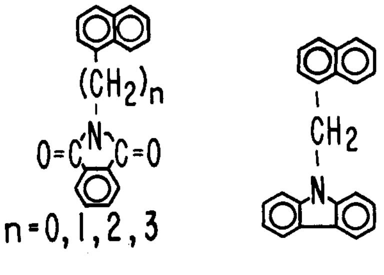
[5] B. Smaller, E. C. Avery, and J. R. Remko, *J. Chem. Phys.*, **43**, 922 (1965).

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

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

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

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



I II

Figure 1. Molecules studied. The compounds are named in the Experimental Section.

matrix is not random, but instead complexes or small crystallites are formed and these species are responsible for the energy transfer. In the molecules studied in this series of papers more definite statements can be made about the geometric relations between the interacting chromophores. It is desirable to be able to observe the spectral properties of the interacting molecules. This is difficult in a random solution because most of the molecules are not interacting, and their properties mask those of the small fraction which are interacting.

The measurements of the fluorescence, phosphorescence, and some of the absorption spectra were made at 77°K in a rigid-glass matrix. This rigid matrix does not permit molecular rotation or diffusion and eliminates transfer mechanisms which involve internal 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.

Absorption Spectra

The absorption spectra discussed in this section were taken on a Cary 14 spectrophotometer. The solvent for the room-temperature spectra was cyclohexane, and the solvent for the 77°K spectra was a mixture of 30% butyl alcohol and 70% isopentane.[10] The low-temperature sample cell had a copper sample holder, in intimate contact with liquid N_2 and quartz windows. The molar extinction coefficients were corrected for an increase in concentration due to solvent contraction by multiplying the concentration at room temperature by 1.26.[11]

The spectra of I, when $n = 0$ and 2, and its separated parts are displayed in Figure 2. These spectra were taken at 77°K. The lower temperature caused a sharpening of the naphthalene spectra but had little effect on the spectra of N-methylphthalimide. The absorption spectrum of I at room temperature in the same solvent did not differ significantly from that shown in Figure 2. It is difficult to be very quantitative when measuring absorption spectra at low temperatures through a rigid-glass matrix because of the uncertainties in the concentration and scattering properties of the glass. The extinction coefficients are considered to be accurate to 25%, based on agreement of spectra of a series of experiments. The positions of the band maxima, however, are quite accurate. Nevertheless, the sum of the two parts agrees very well with the spectrum of the double molecule at wavelengths shorter than 3200 Å. The deviation from additivity in the region where the wavelength is greater than 3200 Å appears to be real and will be discussed later. The spectra of the compounds where $n = 1$ and 3 are very similar to the spectrum shown for $n = 2$.

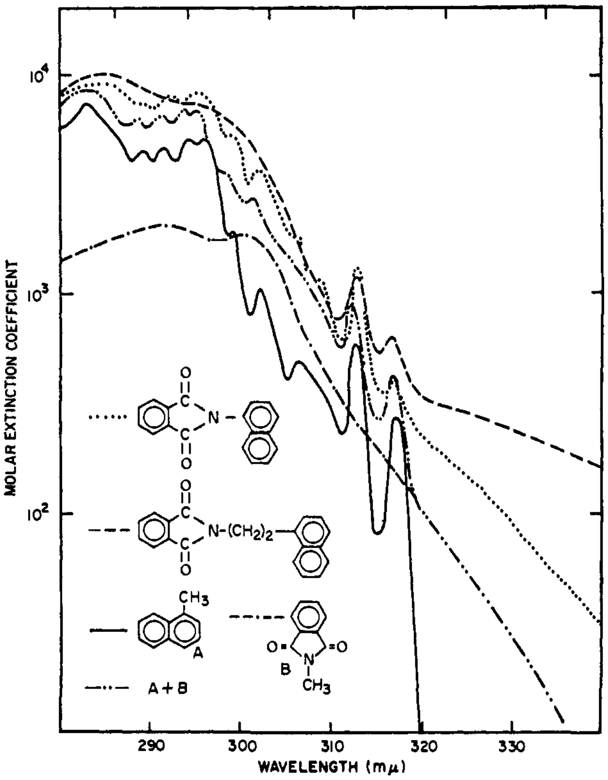


Figure 2. Absorption spectra.

The absorption spectrum of II was found to be the sum of the absorption spectra of N-methylcarbazole and 1-methylnaphthalene at all wavelengths. There was no anomalous absorption at long wavelengths as was reported for I above.

Fluorescence Spectra

Fluorescence spectra were excited with an ac, 200-w Xe lamp. The 120-cycle radiation from this lamp was passed through a large aperture monochromator and onto the sample. The fluorescent 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 the excitation lamp. No attempt was made to correct the spectral intensities for variations in the output of the detector and monochromator with wavelength. All fluorescence measurements were made at 77°K in the rigid matrix described above. Concentrations of solute were typically 10^{-5} *M*.

The lowest excited singlet state of N-methylphthalimide is of n-π^* character and no fluorescence is observed from this molecule. No fluorescence charac-

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[10] The cyclohexane was Spectrograde. The butyl alcohol and isopentane were fluorescent free solvents.

[11] H. E. Rast, Ph.D. Thesis, University of Oregon, 1964.

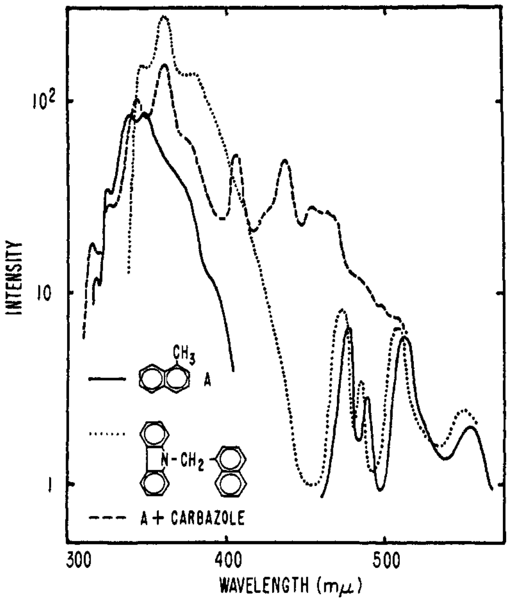

Figure 3. Total luminescence spectra.

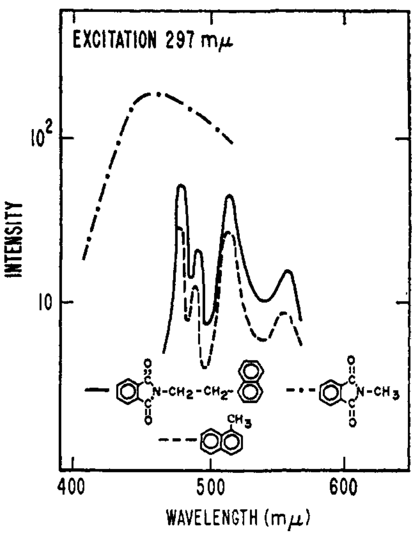

Figure 4. Phosphorescence spectra.

teristic of the naphthalene chromophore was observed from I when the naphthalene chromophore was initially excited. Measurements on equimolar mixtures of naphthalene and phthalimide indicated that if 1% of the energy absorbed by the naphthalene chromophore in I had been radiated as naphthalene fluorescence it would have been detected. This result is interpreted to indicate that the singlet excitation energy is transferred from the naphthalene chromophore to the phthalimide chromophore.

The fluorescence of II, 1-methylnaphthalene, and an equimolar mixture of carbazole and 1-methylnaphthalene are shown in the left of Figure 3. The fluorescence of II is characteristic of carbazole even when the initial absorption is at a wavelength where the naphthalene chromophore absorbs. This result also indicates that the singlet excitation energy is transferred from the naphthalene chromophore to the carbazole chromophore. This is in agreement with the fact that the singlet excitation energy in carbazole is lower than the singlet excitation energy in naphthalene.

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. Visible light was removed from the excitation radiation by the use of a quartz, uv pass filter (Corning 7-54[12]). Two shutter speeds, 20 and 400 cps, were used. The time resolution between excitation and observation at the fast shutter speed is 1.2 msec. The faster shutter was always used when searching for emission from the triplet donor. A 0.5-m Ebert scanning monochromator was placed at 180° from the excitation lamp. Radiation leaving the monochromator was detected with a 1P21 photomultiplier tube and the signal from the photomultiplier passed through an RC circuit with a 1-sec time constant and into a strip chart recorder. All phosphorescence spectra were observed at 77°K in the rigid matrix described above.

The phosphorescence spectra of I ($n = 2$), 1-methylnaphthalene, and N-methylphthalimide are shown in Figure 4. The spectra of I and 1-methylnaphthalene are in excellent agreement. The phosphorescence of N-methylphthalimide is very intense and structureless. In an equimolar mixture of 1-methylnaphthalene and N-methylphthalimide, the naphthalene phosphorescence is completely hidden by the phosphorescence from the N-methylphthalimide. Care was taken to make it possible to compare the intensities of these spectra. At the excitation wavelength (297 mμ) the extinction coefficients of 1-methylnaphthalene and N-methylphthalimide are approximately equal. The intensity of the phosphorescence of I is about twice the intensity of the phosphorescence of 1-methylnaphthalene. This is what would be expected if all of the energy absorbed by the naphthalene and phthalimide chromophore in I were transferred to the naphthalene chromophore and quantum yields were unchanged. (Note: excitation energy can be transferred away from the naphthalene moiety in the singlet system and then back in the triplet system. This pathway for population of the triplet state is completely different from that followed in an isolated naphthalene molecule and permits higher phosphorescent quantum yields because the normal fluorescence is by-passed.) The spectra of I ($n = 1$ and 3) are similar to the spectrum of I ($n = 2$). The phosphorescence of I ($n = 3$) and a mixture of I and N-methylphthalimide are shown in Figure 5. Careful examination of this figure shows that no more than 1% of the phthalimide chromophore is emitting in I. The appearance of the phthalimide emission in the mixture rules out a consideration of intermolecular energy transfer.

The total emission spectra of II, 1-methylnaphthalene, and an equal molar mixture of 1-methylnaphthalene and carbazole are shown in Figure 3. In the equimolar mixture the naphthalene phosphorescence is completely hidden under the carbazole phosphorescence, but the phosphorescent region of II shows only emission from

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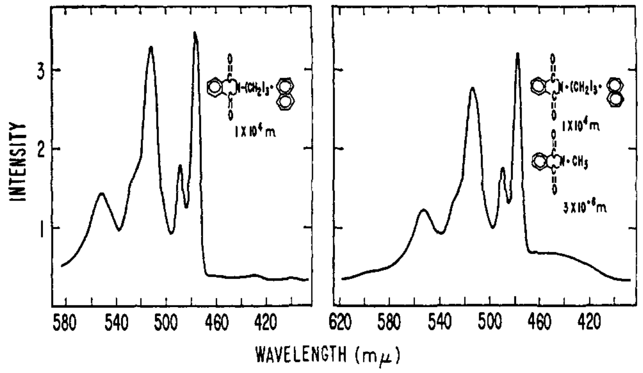
[12] Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.



PHOSPHOROSCOPE 400 CYCLES/sec

Figure 5. Phosphorescence spectra.

the naphthalene chromophore. In contrast to this, all of the fluorescent emission comes from the carbazole chromophore. The fact that the singlet state of the carbazole compound is unaffected by the presence of the naphthalene chromophore proves that the transfer mechanism is from the triplet state of carbazole to the triplet state of naphthalene and not from the singlet state of carbazole to the triplet state of naphthalene. This interesting compound affords the unusual opportunity to observe phosphorescence and fluorescence from two spatially different origins within the same molecule.

Phosphorescence lifetimes were measured by displaying the total phosphorescence decay on an oscilloscope and photographing the decay curve. Time spikes were placed on the same picture by the use of a time mark generator. All decay curves were exponential—a characteristic of the triplet acceptor in the double molecules. The phosphorescence lifetimes are listed in Table I.

Table I. Phosphorescence Lifetimes

Compound	Lifetime, sec	Compound	Lifetime, sec
1-Methylnaphthalene	2.6	I ($n = 1$)	2.4
N-Methylphthalimide	0.70	I ($n = 2$)	2.4
Carbazole	6.6	I ($n = 3$)	2.4
I ($n = 0$)	2.4	II	2.4

Excitation Spectra

The preceding section demonstrated that there was no phosphorescence from the triplet donor chromophore in all of the double molecules studied. With the exception of some intensity measurements discussed above, there was no evidence that the excitation energy was transferred rather than quenched by some unexplained radiationless process. The excitation spectra discussed below eliminate the possibility that a radiationless quenching process occurs and prove that energy transfer actually occurs.

Excitation spectra were recorded by observing the emission intensity at a particular wavelength as a function of the wavelength of the excitation source. The excitation light was made monochromatic by passing the radiation from a high-pressure, 200-w Xe lamp through a large aperture monochromator. The emission intensities were corrected for the variation in excitation intensity with wavelength. The intensity of the excitation system as a function of wavelength was measured by using a fluorescein fluorescent screen which has an emission quantum yield that is independent of excitation wavelength in the region of interest.

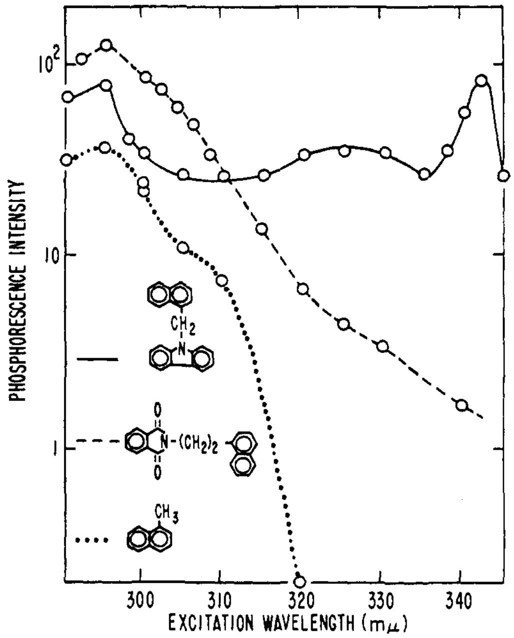


Figure 6. Excitation spectra.

The excitation spectra of dilute solutions of 1-methylnaphthalene, I ($n = 2$), and II are shown in Figure 6. The band pass of the excitation monochromator was about 3 nm for these measurements. The triplet acceptor chromophore in both I and II is naphthalene. Inspection of Figure 6 shows that the naphthalene emission from I and II is excited by long wavelength radiation, which is only absorbed by the triplet donor chromophore in both of these molecules. Similar excitation spectra were obtained for I ($n = 1$ and 3).

Luminescence Spectra

The total luminescence spectra (no rotating shutter) of I, 1-methylnaphthalene, and N-methylphthalimide are shown in Figure 7. The emission in the 400-mμ region was unexpected and is not characteristic of either chromophore. I ($n = 2$) was extensively purified by chromatography over alumina, recrystallization from ethyl alcohol, vacuum sublimation, and zone refining in a nitrogen atmosphere. The ratio of the intensity of the emission at 400 mμ to the intensity of the normal phosphorescence was unchanged by this purification procedure. The emission at 400 mμ was not observable when a phosphoroscope with a time resolution of 1 msec was used. The intensity of the normal phosphorescence and the signal-to-noise ratios of the apparatus indicated that the decay time of the emission was faster than 0.2 msec. This emission was not observable at room temperature. Similar, unexplained emissions were reported for the series of molecules studied by Hammond, *et al.*, in which the two chromophores were benzophenone and naphthalene.[2] II had no emission which was not characteristic of the acceptor chromophore.

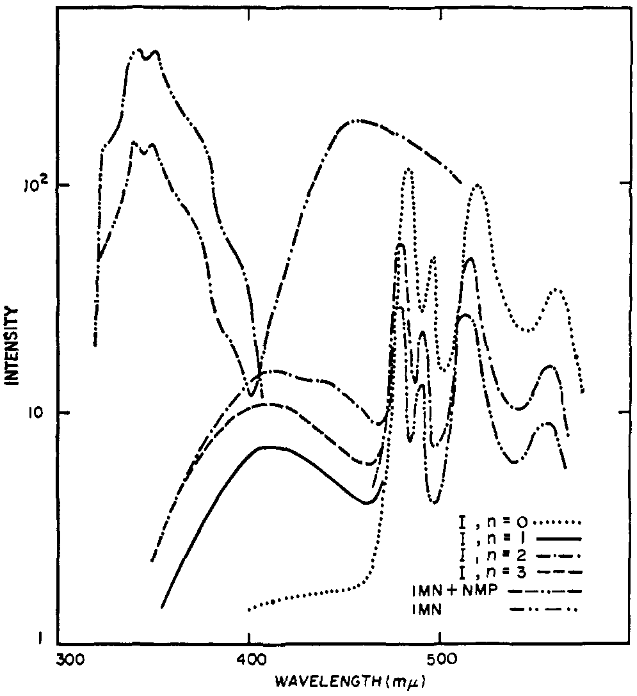


Figure 7. Luminescence spectra: 1-methylnaphthalene (1 MN), N-methylphthalimide (NMP).

In the section on absorption spectra the extra absorption of I in the long-wavelength region was discussed (see Figure 2). In Figure 8, the difference between the extinction coefficient of I and the sum of the extinction coefficients of N-methylphthalimide and 1-ethylnaphthalene is plotted on the same graph with the new emission. There is a good mirror-image relationship between the absorption and the emission, typical of an absorption–fluorescence relationship. Note that this is a one-parameter adjustable fit because the absolute emission intensity is not known. The accuracy of the extinction coefficient in the energy range greater than 32,000 cm^{-1} is very poor because it depends upon a small difference between two very large numbers. Nevertheless, the similarity between the shapes of the two curves is striking.

It is quite possible that this new emission and absorption is charge transfer in nature. When the four aromatic protons on the triplet donor of I were replaced by four chlorines or four bromines, the compounds were found to be highly colored, even though the separate chromophores are colorless. It is well-known[13] that tetrachlorophthalic anhydride forms a charge-transfer complex with naphthalene. The lowest excited electronic state of this complex has an electron distribution with an excess of negative charge around the tetrachlorophthalic anhydride moiety and deficiency of electron charge around the naphthalene moiety. The electronic transition to this excited state results in a broad, structureless absorption band in the blue region of the spectrum and is quite similar to the absorption shown in Figure 2, except that the maximum is at longer wavelengths for the tetrachlorophthalic anhydride complex, as would be expected. The color of the tetrachlorophthalic anhydride–naphthalene complex is

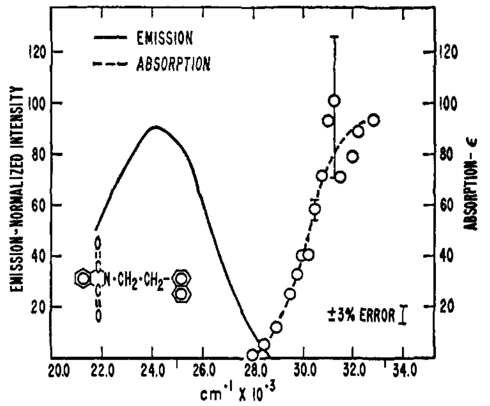


Figure 8. Mirror-image relationship between absorption and emission.

quite similar to I when the four aromatic protons are replaced by four chlorines.

Intermolecular Transfer

Several experiments which attempted to measure the competition between inter- and intramolecular energy transfer are discussed in this section. Intermolecular transfer of triplet excitation energy has been extensively discussed by Ermolaev.[4] When a rigid-glass solution containing a small amount of triplet donor and a large amount of triplet acceptor (0.01–1 M) is irradiated in the absorption region of the donor, emission can be detected from the triplet acceptor.

A competition for the triplet energy of the donor will occur if another molecule, with a triplet energy below that of the donor but above that of the acceptor on the double molecule, is added to a solution of the double molecule. The lowest triplet energy level of fluorene is lower than that of N-methylphthalimide but higher than that of naphthalene.

A mixture of I ($n = 3$) (2×10^{-4} M) and fluorene (1×10^{-2} M) was excited through a Corning O-52[12] filter, and no emission was detectable from the fluorene. The O-52 filter does not pass uv light of sufficient energy to excite either fluorene or naphthalene. Fluorene phosphorescence is clearly visible in a mixture of N-methylphthalimide (2×10^{-4} M) and fluorene (1×10^{-2} M).

Unfortunately, the energy-level schemes are such that it is possible that energy could be passed intermolecularly to the fluorene and then back from the fluorene to the naphthalene. This would also result in no emission from the fluorene. However, the spatial arrangements are such that a large fraction of the fluorene molecules, which are close enough to the triplet donor to receive the triplet energy, are still quite far from the naphthalene and should not be able to transfer energy back to the double molecule. The most probable distance between a donor molecule and an acceptor molecule in a 0.10 M solution is 30 Å. About 5% of the molecules are less than 10 Å apart. Our tentative conclusion is that intramolecular energy transfer is not much slower than intermolecular energy transfer. This is in agreement with what would be expected if strong complexing was not responsible for intermolecular transfer.

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(13) G. Briegleb, "Molekulverbindungen and Koordinationsverbindungen in Einzeldarstellungen. Electron-Donor-Acceptor-Komplexe," Springer-Verlag, Berlin-Wilmersdorf, 1961.

Discussion

The most general conclusion which results from the work described above is that complete transfer of triplet excitation energy occurs from the donor to the acceptor chromophore in all cases studied.

Some of the molecules studied were not structurally rigid (series I), and it is possible that some conformations exist in which the donor and acceptor chromophores are close to each other. However, the important point is that a large number of conformations will exist in which the donor and acceptor chromophores are quite far apart and complete energy transfer occurred from *all* conformers. It is important to make these measurements in a rigid medium because in a fluid medium intramolecular motion will bring both chromophores very close to each other many times during the lifetime of the triplet state. Phosphorescent polarization measurements have shown that large aromatic molecules are held very tightly in the rigid glass used at 77°K, and changes from one conformation to another cannot occur.[14] Molecular models were constructed of the molecules in the I series, and it is possible to twist the models so that the two chromophores are close to each other for all members of the series. Measurements of more reasonable, extended forms of the models indicated that the distance between the chromophores is about 5 Å for I ($n = 3$).

A more complete discussion relating the results of these measurements to the mechanism of triplet excitation energy transfer will follow part III of this series.

Experimental Section

Preparation of Compounds. I ($n = 0$). N,N-Phthaloyl-1-aminonaphthalene. About 3 g of 1-aminonaphthalene and slightly more than 1 equiv of phthalic anhydride were dissolved in 60 ml of glacial acetic acid, refluxed for about 45 min, treated with 450 ml water, brought to a boil, cooled, filtered, and recrystallized from ethyl alcohol to yield white plates, mp 184–185°, lit.[15] 185°.

I ($n = 1$), N,N-Phthaloyl-1-aminomethylnaphthalene. 1-Aminomethylnaphthalene (1 g) and 1 g of phthalic anhydride were dissolved in 10 ml of glacial acetic acid and refluxed for 30 min. The product separated out on cooling. It was chromatographed and recrystallized from heptane–benzene, white powder, mp 179–180°, lit.[16] 175–176°.

I ($n = 2$), N,N-Phthaloyl-1-(1-aminoethyl)naphthalene. The preparation was similar to I ($n = 1$). Recrystallization from an ethyl alcohol–petroleum ether mixture yielded white needles, mp 144–145°, lit.[17] 143°.

I ($n = 3$), N,N-Phthaloyl-1-(3-aminopropyl)naphthalene. The preparation was similar to I ($n = 1$). Recrystallization from an ethyl alcohol–petroleum ether mixture yielded a white crystalline solid, mp 98–99°.

II, N-(Methyl-1-naphthyl)carbazole. This compound was prepared using a special synthesis by Eastman Kodak. Potassium hydroxide was added to carbazole dissolved in tetralin and xylene. Heating to around 165° resulted in the formation of a yellow suspension of carbazolepotassium. The water formed was azeotroped off with xylene. Chloromethylnaphthalene was added and the mixture heated to 170–180°. It is possible to observe the progress of the reaction by the change in the appearance of the precipitate from carbazolepotassium to potassium chloride. After refluxing for several hours, the mixture was cooled, the potassium chloride filtered off, and most of the solvent removed by distillation. The melt was poured into a tray to solidify, washed with ligroin, and recrystallized from benzene. The product was a white powder, mp 152–154° after three recrystallizations from ethyl alcohol. The infrared spectrum showed no NH absorption, indicating reaction had gone to completion.

Acknowledgments. One of the authors (D. E. B.) is grateful to the Chemistry Department of the University of Oregon and the National Bureau of Standards for permission to complete his master's thesis research at the National Bureau of Standards.

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(14) M. A. El-Sayed and R. G. Brewer, *J. Chem. Phys.*, 39, 1623 (1963).

(15) G. Wanag, *Chem. Zentr.*, [II] 3815 (1939).

(16) C. W. Shoppee, *J. Chem. Soc.*, 37 (1933).

(17) S. Rajagopalan, *J. Indian Chem. Soc.*, **17**, 567 (1940).

Intramolecular Energy Transfer between Triplet States of Weakly Interacting Chromophores. II. Compounds in Which the Chromophores are Perpendicular to Each Other[1]

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Contribution from the National Bureau of Standards, Washington, D. C. 20234.

Received May 3, 1967

Abstract: The intramolecular energy-transfer properties between two chromophores held perpendicular to each other by a spiro linkage were investigated at 77°K. Complete transfer of both singlet and triplet excitation energy to the chromophore with the lowest excited state of a particular multiplicity was observed for both of these molecules. No absorption or emission bands were observed which could not be attributed to one of the chromophores.

Lamola, Leermakers, Byers, and Hammond[2] and Breen and Keller[3] found that triplet excitation energy was rapidly transferred from one chromophore to another on the same molecule even when the two chromophores were separated by one, two, and three methylene groups. Although the above measurements were made in a rigid-glass matrix at 77°K to eliminate transfer mechanisms which involve internal molecular motions, the molecules studied were not structurally rigid and it is possible, but not probable, that these

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[1] This research was supported in part by the Advanced Research Projects Agency.

[2] A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2670 (1963); **87**, 2322 (1965).

[3] D. E. Breen and R. A. Keller, *ibid.*, 90, 1935 (1968).