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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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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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).

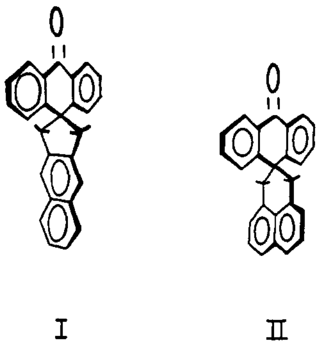

Figure 1. Structure of the molecules studied in this report. Note that the "spiro" linkage holds the rings to the two chromophores perpendicular to each other. These compounds are named in the Experimental Section.

molecules existed in a conformation in which there was a complex formed between the two chromophores.

The transfer properties of the molecules shown in Figure 1 are the subject of this paper. In these molecules the two chromophores are held relatively rigidly at right angles to each other by the spiro linkage at the bridge carbon. These molecules were chosen to examine the effect of the relative orientation of the two chromophores on the transfer properties of the excitation energy.

The orientation of the naphthalene chromophore with respect to the anthrone chromophore differs by 90° in I and II. This means that dipole–dipole coupling between the two groups might be expected to be different for the two molecules and some insight into the mechanism of energy transfer could be obtained.

A detailed discussion of the transfer properties of both singlet and triplet excitation energy in these molecules is given below. Measurements were made at 77°K in a rigid-glass matrix which eliminated a consideration of diffusion mechanisms in the energy-transfer process. 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 measured on a Cary 12 spectrophotometer. The solvent was cyclohexane, and measurements were made at room temperature.

The spectra of I and its two separated parts are displayed in Figure 2. The sum of the two parts agrees very well with the spectrum of the double molecule. In contrast to the molecules discussed in part I[3] of this series and the molecules studied by Hammond, *et al.*,[2] there was no extra absorption at long wavelengths.

The spectrum of II also agreed very well with the sum of the spectra of its two separated parts. Again there was no extra absorption at long wavelengths.

Fluorescence Spectra

Fluorescence measurements were made at 77°K in a rigid-glass matrix.[4] Details of the experimental procedure are given in part I of this series.[3]

Molecules in which the lowest singlet excitation is n → π* typically do not fluoresce but, instead, the excitation energy crosses to the triplet manifold and these molecules have high phosphorescent quantum yields. No fluorescence was observable from a 1×10^{-4} *M* solution of either I or II under conditions where the fluorescence of a 2×10^{-5} *M* solution of 2,3-dimethylnaphthalene was at least 100 times greater than the noise level of the apparatus. Intermolecular transfer of excitation energy away from the naphthalene chromophore is unimportant at this concentration. These results indicate that no more than 1% of the naphthalene chromophores, which are initially excited, emit.

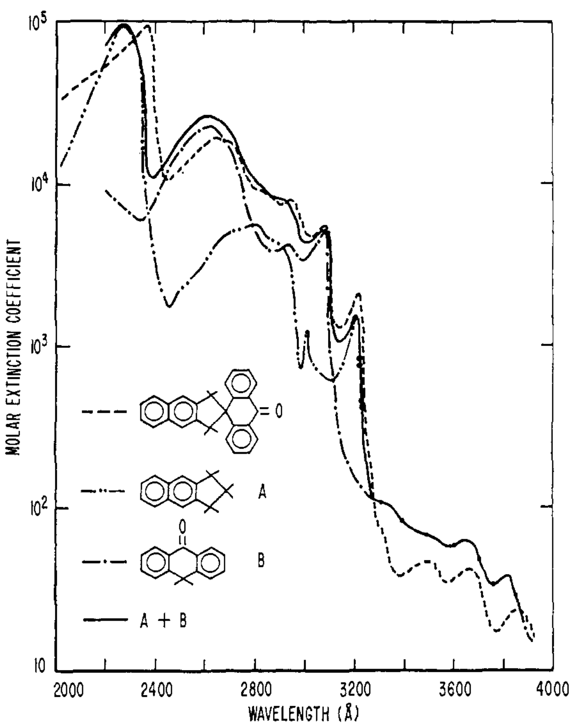

Figure 2. Absorption spectra.

Phosphorescence Spectra

Phosphorescence measurements were made at 77°K in the rigid-glass matrix described above.[4] Details of the experimental procedure are given in part I of this series.[3]

The phosphorescence spectrum of I and the spectrum of 5,6-benzindan are shown in Figure 3. The agreement between the two spectra shows that the phosphorescence is characteristic of the naphthalene chromophore. This is also the case with II.

The phosphorescence of I and a mixture of I and anthrone are shown in Figure 4.[5] Careful examination of this figure shows that no more than 1% of the anthrone chromophore is emitting in I. At the same time, the appearance of the anthrone emission in the mixture rules out the possibility that the energy transfer observed in I is intermolecular in nature. Similar experiments with II and mixtures of II and anthrone show

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(4) 30% butyl alcohol and 70% isopentane.

(5) The lifetime of the anthrone chromophore is in the millisecond region and close to the rotational time of the phosphoroscope. The radiationless transfer of the triplet excitation energy from the anthrone chromophore to the naphthalene adds another term to the first-order decay constant of anthrone and reduces its lifetime. In order to say that less than 1% of the anthrone chromophore is emitting, it is necessary to use a phosphoroscope with a time resolution of 1/100th of the lifetime of anthrone. Since this was not practical, the rotating phosphoroscope was removed and the total luminescence was observed. This, in effect, provided infinitely fast time resolution.

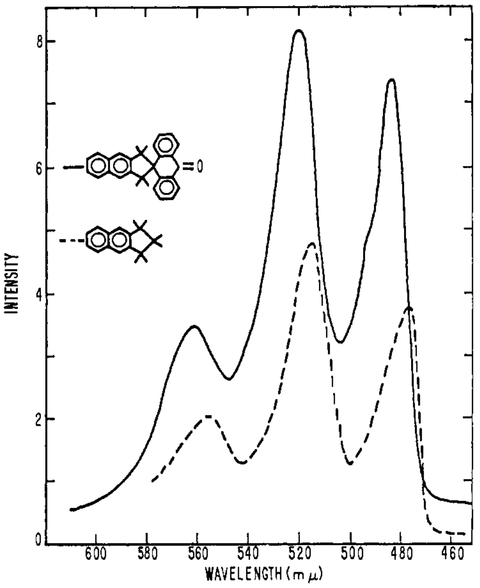

Figure 3. Phosphorescence spectra.

that the anthrone chromophore is emitting no more than 1% of its usual emission in these compounds.

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 and characteristic of the triplet acceptor in the double molecules. The phosphorescence lifetimes are listed in Table I.

Table I. Phosphorescence Lifetimes

Compound	Lifetime, sec
I	2.3
II	2.2
Anthrone	1.4×10^{-3} [a]
5,6-Benzindan	2.6
Naphthalene	2.2

[a] Measured on a sample which had an impurity present (perhaps anthranol). The 1.4-msec emission constituted over 90% of the total emission.

Excitation Spectra

The preceding section demonstrated that there was no emission from the donor chromophore in all of the double molecules studied. This does not prove 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.

The lowest excited singlet state of anthrone is of n → π* character and of relatively low energy compared to the lowest excited singlet state of naphthalene. It is possible to excite the anthrone chromophore in I and II with lone-wavelength radiation that will not be absorbed by the naphthalene chromophore. A 2.5-cm solution filter containing a concentrated naphthalene in cyclohexane solution (12.8 g/l.) was used in addition to a quartz uv pass filter to excite I and II. Phosphorescence was clearly visible, while no phosphorescence was visible from a solution of 2,3-dimethylnaphthalene excited through the same filter.

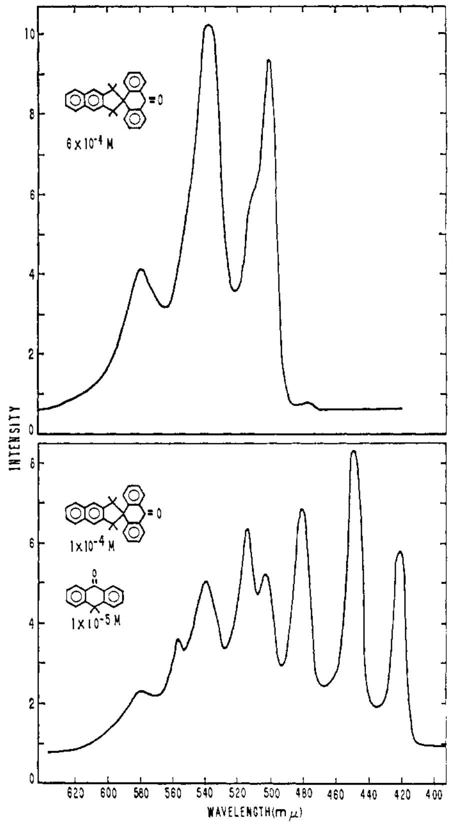

Figure 4. Phosphorescence spectra.

Some experiments were done with mixtures of II and anthrone to attempt to determine the *approximate* efficiency of the triplet energy-transfer process. The phosphorescence spectra of a solution 1×10^{-4} M in II and 1×10^{-5} M in anthrone were excited through the same filter solution so that only the anthrone chromophore was excited in both species. The emission from the anthrone was 0.3 times as intense as the emission from II. After multiplication of the ratio of intensities by 10 because of the difference in concentration, the data indicate that the phosphorescent quantum yield of II is about one-third the phosphorescent quantum yield of anthrone.

The phosphorescent quantum yield of anthrone is almost 1; this means the quantum yield of II is about 0.3. It is difficult to predict what the quantum yield of II should be, because the quantum yield of perinaphthane is not known. However, 0.3 seems to be slightly high because the quantum yield of naphthalene is only 0.1 and both compounds have similar lifetimes (see Table I). The data show that little of the triplet excitation energy of the anthrone chromophore is lost during the transfer to the naphthalene chromophore.

A similar comparison of the intensities of the phosphorescence of a mixture of I and anthrone indicates that the quantum yield of I is about 0.1. Again, little, if any, energy is lost during the transfer.

Luminescence Spectra

In part I[3] of this series and in the work of Hammond, *et al.*,[2] some emission and absorption not characteristic of either chromophore were observed in molecules in which a naphthalene chromophore was isolated from a benzophenone or phthalimide chromophore by a series of methylene groups. This emission and absorption were attributed to charge transfer from the naphthalene chromophore to the acceptor chromophore.

Similar emission and absorption were searched for in the case of I and II, but none was found. The energetics of the chromophores present in I and II are similar to those discussed above. The perpendicular orientation of the chromophores in I and II must prohibit the formation of a low-lying electronic state which is largely charge transfer in origin.

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.[6] 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 a 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 anthrone but higher than that of naphthalene.

A mixture of I (2×10^{-4} *M*) and fluorene (1×10^{-2} *M*) was excited through a Corning O-52[7] filter and no emission was detectable from the fluorene (see Figure 5). The O-52 filter does not pass uv light of sufficient energy to excite either fluorene or naphthalene. Also shown in Figure 5 is the emission spectrum of a mixture of anthrone (2×10^{-4} *M*) and fluorene (1×10^{-2} *M*). In this case the fluorene emission is clearly visible. The sensitivity of the apparatus is the same for both systems. The time resolution of the phosphoroscope was only 0.03 sec and not fast enough to detect anthrone phosphorescence. Similar measurements with mixtures of II and fluorene also showed that there was no intermolecular transfer between the double molecules and fluorene.

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 0.01 *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 in I and II. This is in agreement with what would be expected if strong complexing was not responsible for intermolecular transfer.

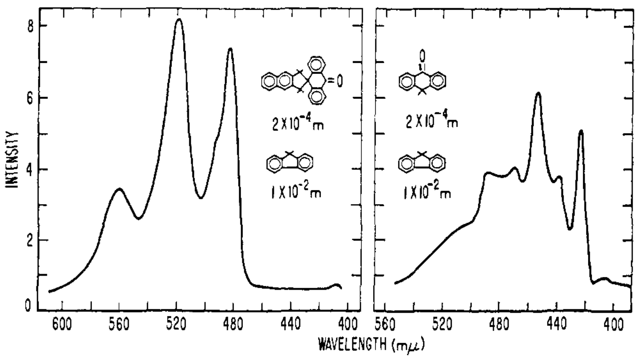

Figure 5. Phosphorescence spectra.

Discussion

In I and II the excitation energy was always transferred to the chromophore with the lowest excitation energy in both the singlet and triplet systems. Within the limits of experimental error no emission was detected from the donor chromophores which indicates that the transfer was essentially (>99%) complete. Excitation spectra prove that the energy was transferred rather than lost by a radiationless process.

In molecules I and II the π systems of the moieties are perpendicular to each other and the transition vectors oriented in such a way that, in the absence of molecular distortion or vibronic interactions, the dipole–dipole coupling between the chromophores is zero. The transition vector for the lowest excited singlet state of naphthalene lies along the long axis of the molecule. The lowest excited singlet state of anthrone is of $n \rightarrow \pi^*$ character and belongs to the $^1A_2$ representation in C_{2v} symmetry. In the absence of molecular distortion or molecular vibrations, there are no electric dipole matrix elements connecting this state with the ground state, and the transition vector is zero. Shimada and Goodman have found that vibronic coupling is responsible for the observed transition and the transition vector is perpendicular to the carbonyl bond and in the molecular plane.[8] This vibronically induced transition vector of the lowest excited singlet state of the anthrone chromophore is perpendicular to the plane of the naphthalene chromophore and hence perpendicular to all $\pi \rightarrow \pi^*$ vectors in both I and II. The transition vector to the lowest vibrational level is zero and no $0 \rightarrow 0$ transitions are observed in absorption.[8] At low temperatures, when only the lowest vibrational level is populated, no dipole–dipole coupling can exist between the anthrone chromophore and the naphthalene chromophore. Dipole–dipole coupling can exist in higher vibrational levels through the mechanism of vibronic interactions; however, this should be a small effect because the principal vibronic coupling scheme present in the anthrone chromophore still results in a transition vector which is perpendicular to the naphthalene ring (see above). If vibrational excitation is responsible for energy transfer, then it would be expected that the transfer time would

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

[7] 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.

[8] R. Shimada and L. Goodman, *J. Chem. Phys.*, **42**, 790 (1965); 43, 2027 (1965); W. D. Chandler and L. Goodman, *ibid.*, **45**, 4088 (1966).

be strongly temperature dependent. The transfer properties of these molecules will be investigated at liquid helium and liquid hydrogen temperatures and will be reported on at a later date.

Another possible mechanism, besides vibrational excitation and vibronic coupling, for permitting dipole–dipole coupling between the two systems is molecular distortion. As long as the anthrone chromophore remains planar, the transition vector to the lowest vibrational level is zero and there is no dipole–dipole coupling between the two chromophores even if molecular distortion causes the two chromophores to be not perpendicular to each other. If the coupling mechanism involves vibrational excitation and vibronic coupling, a small deviation from a 90° angle between the two rings will permit the principal vibronic interaction discussed above to couple the two chromophores. Distortions of the plane of the anthrone chromophore result in a nonzero transition moment to the lowest vibrational level and open the possibility of dipole–dipole coupling between the chromophores.

The general conclusion of the above discussion is that it is unlikely that dipole–dipole coupling is responsible for the interaction between the singlet states of the two chromophores in I and II. This means that it is also unlikely that the coupling scheme between the triplet states of these chromphores is a combination of spin–orbit coupling and dipole–dipole coupling between the lowest singlet systems. Coupling schemes involving higher excited singlets in the anthrone chromophore, which can couple directly with naphthalene states, are still a possibility, but the probability of this is reduced because of the large energy difference between these states. In contrast to the Coulomb integrals which lead to the dipole–dipole coupling scheme,[9] the exchange integrals which connect the states of the interacting chromophores are not very dependent upon the orientation of the chromophores. This fact might lead to an experimental method for distinguishing between these two mechanisms.

The evaluation of exchange integrals between two separated chromophores is very difficult because the answer is strongly dependent upon the value of the molecular wave functions at large distances from the atomic centers. Unfortunately, our knowledge of the wave functions in this region is very limited.

A more complete discussion of the mechanisms possible for the transfer of excitation energy as related to the experimental observations will be included in part III of this series.

Experimental Section

Spiro[9,10-dihydro-9-oxoanthracene-10,2′-5′,6′-benzindan] (I), a white powder, mp 223.0–223.5° was prepared by distilling 15 ml of methanol onto 0.4 g of clean lithium metal in an inert atmosphere. Anthrone (2.4 g) in toluene (15 ml) was added to the white slurry, and the resulting brown solution was poured slowly (10 min) into a refluxing dioxane solution of 3.4 g of 2,3-bis(bromomethyl)naphthalene. The mixture was refluxed at 80° for 150 min after which time an aliquot spotted on a thin-layer chromatogram showed no unreacted bromomethylnaphthalene and the reaction was stopped by the addition of cold water. The organic phase was evaporated to dryness and chromatographed on activity IV alumina. The product was eluted with 20% benzene in heptane; a 0.9-g fraction was recrystallized from pyridine–water and from benzene–light petroleum. Sublimation at 190° (10^{-2} torr) yielded 100 mg of material.

Anal. Calcd: C, 90.1; H, 5.2. Found: C, 89.6; H, 5.1.

Spiro[9,10-dihydro-9-oxoanthracene-10,2′-(3′H) phenalene] (II), white powder, mp 223–225° was prepared similarly to I, yield 0.1 g.

Anal. Calcd: C, 90.1; H, 5.2. Found: C, 90.4; H, 4.9.

Acknowledgments. The author is grateful to Mr. J. J. Natterstad for the synthesis of these compounds.

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[9] The approximation of the Coulomb integrals by a coupling between the transition vectors is only a good approximation when the overlap of the two molecular wave functions is small. The lowest singlet state of the anthrone chromophore is predominantly localized on the carbonyl group which is approximately 6–8 Å away from the naphthalene chromophore. This should lead to small overlap between the molecular wave functions and validate the approximation used here.