solved in 20 ml of tetrahydrofuran, the mixture was cooled to 0°, and 5.0 ml of methanol (122 mmol) was slowly introduced. There was a vigorous reaction and 92.5% of the theoretical hydrogen was evolved by the time the addition had been completed. The solution was stirred at room temperature for 2 hr. The total hydrogen evolved increased to 98.5% of the calculated quantity.

The flask was immersed in an oil bath and the temperature raised to 165° as the tetrahydrofuran and possible B-methoxyborolane was collected. However, glpc examination of the distillate revealed only traces of B-methoxyborolane.

The flask containing the product was connected to a vacuum and heated. At 85–90° bath temperature and a pressure of 15 mm, distillation of a volatile product was observed and 2.82 g was collected in a trap cooled to −78°. Glpc analysis showed the presence of solvent (15%) and two peaks with retention times of 3.8 and 6.2 min. By raising the bath temperature to 180–200°, a larger fraction was collected, 3.58 g. Glpc analysis showed the presence of B-methoxyborolane, 62%, retention time 2.0 min, and the previous two peaks of longer retention time, 3.8 and 6.2 min.

Reaction of the 1:1 Dimer with Methanol. Freshly distilled 1:1 dimer, 5.73 g, 42.1 mmol, was dissolved in 15 ml of tetrahydrofuran at 0° and 5.0 ml of methanol (122 mmol) added. There was an initial evolution of 80 ml of hydrogen (3.57 mmol, 4.25%). Further evolution was very slow, the total being 97 ml (5.13%) after 24 hr. The solution was then refluxed for 24 hr, causing the slow liberation of 1380 ml of hydrogen (61 mmol, 73% of theory[8]). Glpc analysis showed the presence of 18% unreacted 1:1 dimer.

The tetrahydrofuran was removed at atmospheric pressure. Depolymerization with vacuum distillation gave two fractions: 3.62 g, with one major peak (70%) on glpc examination, exhibiting a retention time of 2.5 min, and three minor peaks with retention times of 5.2, 8.2, and 14 min, and 2.42 g, with glpc showing the presence of six peaks. Redistillation of the larger first fraction at atmospheric pressure, bp 92–96° (747 mm), yielded 2.14 g. However, glpc analysis showed no improvement in apparent purity. Nevertheless mass spectral examination of this fraction showed one parent peak at low voltage (15 eV) at m/e 97 and 98, in accordance with that expected for B-methoxyborolane.

In another experiment, n-dodecane was added as an internal standard and the reaction followed by glpc analysis, as well as by hydrogen evolution. The 1:1 dimer, 1.33 g (9.8 mmol), freshly distilled in 4.0 ml of tetrahydrofuran containing 0.725 g of n-dodecane. Then 1.0 ml (24 mmol) of methanol was added, causing the liberation of 18 ml of hydrogen (0.80 mmol, 4.1%) in 85 min. The solution was brought to a gentle reflux and the evolution of hydrogen was observed as samples were removed with a syringe for glpc examination. The results are shown in Figure 2.

Protonolysis of the 1:1 Dimer. Freshly distilled dimer, 1.44 g, was dissolved in 10 ml of glacial acetic acid at room temperature. No gas was evolved. The solution was brought to reflux temperature and maintained there for 4 hr. There was evolved 490 ml of gas. The solution was evaporated to dryness *in vacuo* and 5.0 ml of diethanolamine added, followed by the addition of n-octane. The n-octane was distilled until the distillate showed no trace of acetic acid (1:1 n-octane–acetic acid azeotrope boils at 109°). The residue was treated with acetone, precipitating 338 mg (1.08 mmol) of 1,4-butanediboronic acid bisdiethanolamine ester, mp 244–250°. Four recrystallizations from Cellosolve gave the analytically pure sample, mp 261–263° (lit.[11] 245–247°).

Anal. Calcd for $C_{12}H_{26}B_2N_2O_6$: C, 50.74; H, 9.22; N, 9.86. Found: C, 50.91; H, 9.43; N, 9.60.

The 60-Mcps nmr spectrum in D_2O shows two distinctive multiplets centered at δ 3.0 (8 H) and 3.82 (8 H), two broad peaks centered at 0.6 (4 H) and 1.3 (4 H), and an enlarged water peak resulting from the exchange of the NH hydrogens. The infrared spectrum shows a band at 3144 cm^{-1}, characteristic of the NH grouping in diethanolamine esters of boronic acids.[23]

Reaction of the 1:1 Dimer with β-Dimethylaminoethanol. The freshly distilled 1:1 dimer, 0.711 g (5.22 mmol), was dissolved in 4.0 ml of dry tetrahydrofuran and 0.930 g (10.45 mmol) of β-dimethylaminoethanol was introduced with a syringe. There was an immediate evolution of hydrogen corresponding to 85% of the calculated amount. Removal of the solvent gave an oil which could not be crystallized.

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Intramolecular Triplet–Triplet Energy Transfer between Nonconjugated Chromophores with Fixed Orientation[1]

Nicolae Filipescu, John R. DeMember, and Fredrick L. Minn

Contribution from the Department of Chemistry, The George Washington University, Washington, D. C. 20006. *Received August 12, 1968*

Abstract: Efficient but not total triplet–triplet energy transfer is reported between tetralin-1,4-dione and fluorene chromophores held together by a rigid molecular frame at known separation distance and mutual orientation. The exchange mechanism is compared with the alternative resonance-type interaction of admixed singlet character in the lowest triplets. An order-of-magnitude calculation of the exchange-transfer probability gives a result compatible with the observed transfer efficiency.

Triplet–triplet energy transfer is a basic process in both photochemistry and molecular spectroscopy. It was first observed in rigid solutions in which the donor and acceptor molecules were present as cosolutes at 77°K, when selective excitation of the donor led to phosphorescence emission from the acceptor.[2,3] Later, flash spectroscopy allowed observation of the phenomenon in fluid solution at room temperature by determination of the T–T absorption of the acceptor.[4] Other efficient ways to investigate the migration of triplet energy in solution were provided by the use of α-diketones[5,6] or lanthanide-ion acceptors,[7–9] which exhibit quantitatively measurable luminescence in fluid solution corresponding to transitions involving a change of multiplicity of two.

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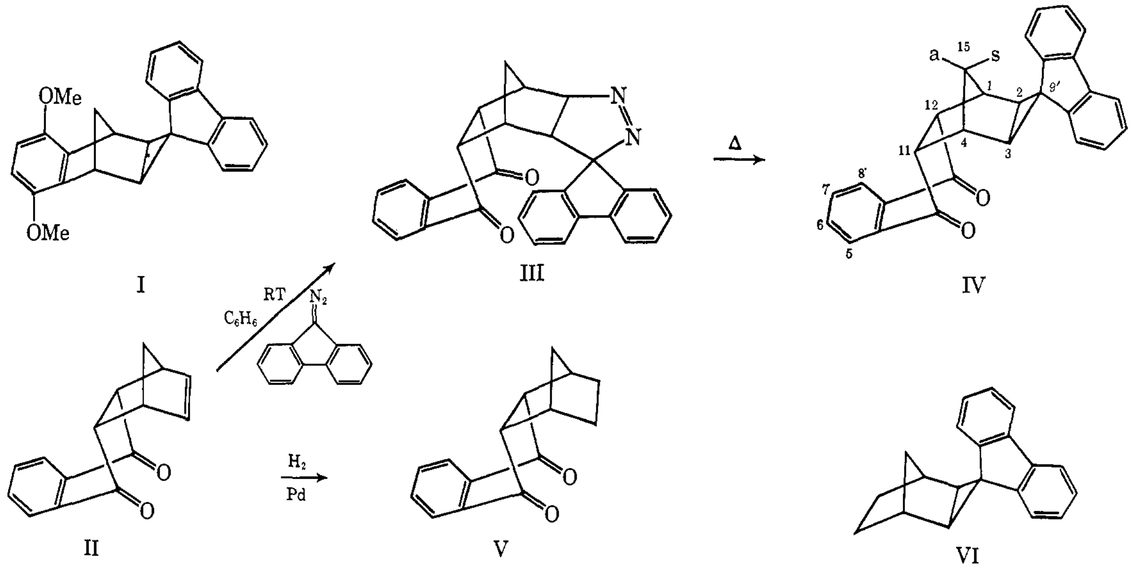
Triplet–triplet energy transfer is presumably due to an exchange mechanism which requires spatial overlap of donor and acceptor orbitals.[10] Therefore, the probability of triplet energy transfer should decrease exponentially with donor-acceptor separation distance and should depend on relative orientation of the two chromophores. A vaguely defined "sphere of quenching" or "active volume" has been postulated to account for T–T energy transfer observed[3] at average separation distances of 15 Å.

Scheme I



A preferential donor–acceptor orientation has been reported in only one case for the benzophenone–phenanthrene-d_{10} pair at 77°K.[11] As in most previous work, the two chromophores had random geometrical distribution and photoselection[12] had to be used to evaluate orientation. Considerable concentration depolarization in both donor and acceptor molecules and admitted possibility of association might have made the results inconclusive. Several attempts have been made to investigate electronic energy transfer between nonconjugated chromophores incorporated in the same molecule.[13–17] Inflexible molecular systems present the advantage of known donor–acceptor separation distance and mutual orientation.

Although the two chromophores in rigid compound I are less than 10 Å apart, we previously found that neither singlet nor triplet transfer could be detected. The absorption and emission spectra of the two π systems were very similar to those of a dilute mixture of separated chromophores.[18] The lack of triplet–triplet transfer was intriguing since the two chromophores were well within the reported T–T interaction distances of 15 Å. It strongly suggested either that these distances were inaccurate or that an orientation effect was responsible for the lack of both singlet–singlet and triplet–triplet transfer. Presently we report evidence for intramolecular triplet energy migration between tetralin-1,4-dione (D) and fluorene (F) chromophores in compound IV (Scheme I). To our knowledge, this is the first report of triplet–triplet energy transfer between two chromophores whose separation and relative orientation are accurately known. In addition, the magnitude of the separation places the two interacting chromophores at a critical distance between molecular contact (collision) and separations much larger than molecular diameters.

Results

Model compound IV was prepared by addition of 9-diazofluorene to olefin II and subsequent thermal decomposition of the resulting 1-pyrazoline III. The steric configuration of IV was derived from the nmr spectrum and confirmed by its uv absorption. The nmr spectrum was found to be similar to that of other spirocyclopropanes known to have *exo* orientation.[19] Molecular models (Dreiding) of IV in which F is *endo* with respect to the norbornene frame suggest that the pronounced overlap of the F and D π systems should be reflected in the uv spectrum. Instead, the absorption of IV was very similar with that of an equivalent mixture of V and VI, consistent with an *exo* orientation of F. The known *endo* positioning of D in the Diels–Alder adduct II is maintained in IV. Of the two possible *endo* conformers, the nmr spectra indicate that the products contain only that conformation shown in Scheme I for compounds II–V. Chemical shifts of norbornene vinyl protons in the nmr and similarity in uv absorption spectra of II and V indicate absence of benzene–olefin transannular interaction expected in the alternate conformer. Elemental analysis and ir and nmr spectra were consistent with structures displayed in Scheme I.

The excitation and emission spectra of F and D chromophores separately attached to the norbornane frame are displayed in Figure 1. A 10^{-3} *M* solution of VI in ether–isopentane–ethanol (EPA) glass at 77°K showed both fluorescence (λ_{max} 320 mμ) and phosphorescence (λ_{max} 460 mμ) whereas diketone V in the same conditions

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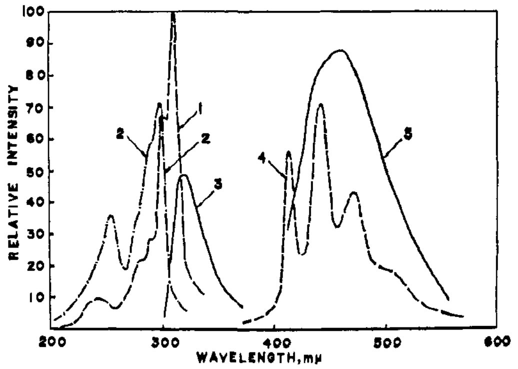

Figure 1. Excitation and emission spectra of separated chromophores, 10^{-3} *M* in EPA at 77°K: (1) excitation of F phosphorescence in VI (emission at 427 mμ), (2) exictation of D phosphorescence in V (emission at 440 mμ), (3) fluorescence of VI excited at 310 mμ, (4) phosphorescence of V excited at 297 mμ, and (5) phosphorescence of VI excited at 310 mμ. Relative intensities refer to each curve separately.

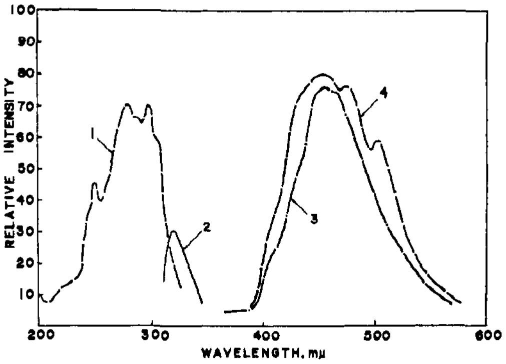

Figure 2. Excitation and emission spectra of model compound IV, 10^{-3} *M* in EPA at 77°K: (1) excitation of phosphorescence at 454 mμ, (2) fluorescence excited at 265 mμ, (3) phosphorescence excited at 304 mμ, and (4) phosphorescence excited at 251 mμ. The intensity units are valid only for each curve separately.

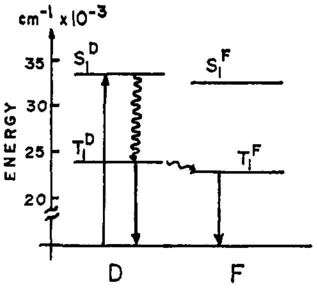

Figure 3. Energy level diagram for F and D chromophores in compound IV; selective absorption at 251 mμ.

exhibited only characteristic carbonyl phosphorescence (λ_{max} 414, 442, 471, and 510 mμ).

The phosphorescence and excitation spectra of one-to-one mixtures of V and VI in EPA at 77°K revealed no interaction between the two chromophores in the 10^{-5}–10^{-3} *M* concentration range. Each chromophore was selectively excited and displayed its characteristic phosphorescence.

Figure 2 shows the emission and excitation spectra of model compound IV in rigid matrix at 77°K. The relatively weak F fluorescence at 320 mμ was virtually unchanged with respect to that of the isolated chromophore. Regardless of excitation wavelength, the phosphorescence spectrum of model compound IV was almost identical with that of isolated F chromophore in VI. Even upon selective excitation of the D chromophore in IV at 251 mμ, the $T_1 \rightarrow S_0$ emission closely resembled the phosphorescence from VI with only a minor contribution from D (curve 5, Figure 2).

Discussion

The 0–0 vibrational bands in the phosphorescence spectra of isolated chromophores locate the first excited triplet states of D and F at approximately 24,000 and 23,000 cm^{-1}, respectively. The excitation spectra suggest the same order for the $v = 0$ levels of lowest excited singlets, namely about 33,600 cm^{-1} for D and 32,700 cm^{-1} for F (see Figure 3).

Singlet–Singlet Interaction. Apparently the two chromophores in compound IV are noninteracting entities in their ground and first excited singlet states. This is shown by the mentioned $\epsilon_{IV} = \epsilon_V + \epsilon_{VI}$ extinction coefficient additivity and by virtually identical fluorescence quantum efficiency of F in IV and in dilute V + VI mixtures. Absence of S–S resonance transfer from D to F in IV and in 10^{-5}–10^{-3} *M* one-to-one mixtures of V and VI suggests that intersystem crossing in diketone D is faster than inductive coupling to the S_1 state of F. An apparent alternative for lack of S–S interaction between the two chromophores at close distance in IV may be the mutual perpendicularity of the $S_0^F \leftrightarrow S_1^F$ and $S_0^D \leftrightarrow S_1^D$ transition moments. The π systems of F and of the benzene nucleus of D are mutually perpendicular in IV. Polarized absorption and emission measurements suggested that the transition vector for $\pi \rightarrow \pi^*$ singlet–singlet transitions in aromatic hydrocarbons lies in the molecular plane. Assuming that the first excited singlet state of D is primarily localized in the plane of the aromatic ring, the mutual orientation of the two $S_0 \leftrightarrow S_1$ vectors could be, as in I, perpendicular. At the same time, the angle made by the transition vector in F with the interconnecting line would be 90 ± 5°.[6] This orientation would be enough to determine a vanishingly small value for the resonance interaction term in the absence of vibronic coupling or molecular distortions. However, since the lowest excited singlet state of D is probably n,π^*, the assumption that the transition moment of $S_0^D \leftrightarrow S_1^D$ is in the plane of the aromatic ring of D is not justified. That $S^D \rightarrow S^F$ transfer does not take place to any significant extent is proved by the large decrease in Φ_f^F/Φ_p^F in IV compared to the value in VI. Approximate calculations using integrated areas under corrected emission spectra gave Φ_f^F/Φ_p^F values of 0.6×10^{-2} for VI and 0.5×10^{-2} to 10^{-3} for IV depending on the excitation wavelength. If D → F transfer in IV would occur primarily at the excited singlet level, Φ_f/Φ_p for the fluorene chromophore would remain essentially unchanged (see Figure 3).

Triplet–Triplet Transfer. The phosphorescence and fluorescence excitation spectra of compound IV displayed in Figure 2 clearly reveal efficient tripletenergy migration from D to F. The transfer efficiency, calculated from data obtained on excitation with light of 251 mμ (where $\epsilon_D^{251} = 12{,}000$ and $\epsilon_F^{251} = 6000$ l. mol^{-1} cm^{-1}), was 83 ± 5%. The two chromophores in compound IV are less than 10 Å apart in a fixed orientation at a distance intermediate between independent separation and collision. Since triplet sensitization

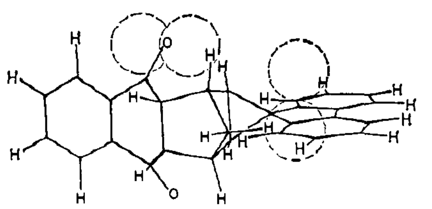

Figure 4. Stereographic view and D–F overlap in compound IV. The nonbonding 2p orbital of the carbonyl oxygen represents the edge of the T chromophore closest to F. Conversely, the 2p orbital on fluorene carbon atom 1 is nearest to D.

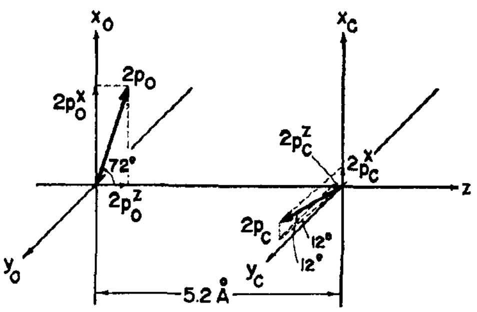

Figure 5. Relative orientation of the n orbital of oxygen ($2p_O$) and the 2p orbital of nearest carbon in fluorene ($2p_C$).

from carbonyl donors is known to occur in solution with a rate close to the diffusion-controlled value,[6,20–22] it seems appropriate to compare the molecular system of IV with a collision situation.

The term *collision* for two separate particles in solution is normally associated with encounters between two neighboring solute molecules within a solvent cage. The average number of individual encounters which such neighboring solute molecules undergo in ordinary organic solvents before they separate to distances outside the collisional state is estimated to be between 10 and 100.[23] Since these encounters between a donor and a neighboring acceptor molecule take place in a variety of random relative positions, all orientation parameters are essentially removed.

Ermolaev and coworkers have claimed that triplet–triplet energy transfer took place in rigid matrix in solutions in which the separated donor and acceptor molecules were at average separation distances of up to 15 Å. However, we believe that the concept of average separation distance, well defined for dilute solution in which no complexation or other type of association occurs, is rather misleading at very high concentrations at 77°K. Polar interactions and microcoprecipitation cannot be ruled out at such close proximity and low temperatures. In addition, the heat liberated by radiationless transitions from excited solute molecules may cause local melting of the glass matrix and thus decrease the actual distances of approach with respect to the values calulated assuming random distribution.[24].

The "active volume" concept first proposed by Perrin for sensitized fluorescence[25] seems to account for some of the cosolute triplet–triplet transfer experiments.[3] However, since it is based on the assumption that molecules are spherical and in a random Herzian distribution, it is obviously inadequate for the much better defined molecular system IV.

Except for vibronic deactivation of electronically excited chromophores, the connecting saturated frame in IV is not expected to be instrumental in the T–T transfer mechanism, since its excited electronic energy levels are essentially localized in the σ bonds and at least 15,000 cm^{-1} above those of the chromophores (see below, however). It is clearly shown that the rigid glass solvent does not play a role in triplet–triplet transfer.[26]

Figure 4 shows the stereographic view of compound IV. The oxygen atoms of the carbonyl groups and the 1′ (or 8′) carbon atom of fluorene represent the edges of the D and F chromophores nearest to each other. The distance between the O and $C_{1'}$ atoms is 5.2 Å. The closest orbital parts of the two chromophores are the nonbonding 2p orbital on oxygen and the 2p orbital on the aromatic carbon 1′.

An order-of-magnitude calculation of the transfer probability by an exchange mechanism can be made using Dexter's expression[10]

$$P_{D^*\rightarrow A^*} = (2\pi/h)Z^2\int_0^\infty F_D(E)\epsilon_A(E)dE$$

where $\int_0^\infty F_D(E)\epsilon_A(E)dE$ represents the donor-emission (T → S_0) − acceptor-absorption (S_0 → T) overlap (in eV)$^{-1}$ and

$$Z^2 = \sum_I\sum_F(g_Dg_AK^2)^{-1}\left|\int\Psi_I(e^2/r_{12})\Psi_F d\tau\right|^2$$

g being the vibrational degeneracy, K the dielectric constant, and I and F referring to the initial and final states, respectively. Using the asterisk to denote the excited electronic state, Φ for the electronic part, and χ for the vibrational part, the initial and final state wave functions are given by $\Psi_I = \Phi_{D^*}\Phi_A\chi_{D^*}\chi_A$ and $\Psi_F = \Phi_D\Phi_{A^*}\chi_D\chi_{A^*}$. Separating the electronic and vibrational integrals, we obtain

$$Z^2 = K^{-2}\left|\sum_I\sum_F g_D^{-1}g_A^{-1}\int\chi_{D^*}\chi_D\chi_{A^*}\chi_A d\tau\right|^2 \times \left|\int\Phi_{D^*}^{(1)}\Phi_A^{(2)}(e^2/r_{12})\Phi_D^{(2)}\Phi_{A^*}^{(1)}d\tau\right|^2$$

An estimate of the exchange integral was obtained using Mulliken's approximation[27] for $\Phi_{A^*}^{(1)}\ \Phi_{D^*}^{(1)}$ and $\Phi_A^{(2)}\ \Phi_D^{(2)}$, Pople's point-charge approximation[28] for the resulting two-center coulomb integrals, and an adaptation of Pariser's approximation[29] for the one-center coulomb integrals. Apparently, other approximate methods of calculation do not change the order of magnitude.[30] With a core-separation distance of 5.2 × 10^{-8} cm, the orientation shown in Figure 5, and con-

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sidering the fact that there are two equivalent carbonyl oxygens, the calculated exchange integral is of the order of 10^{-11} eV. Assuming a Franck–Condon factor[31] of roughly 10^{-1}, one obtains $Z^2 \sim 10^{-26}$ eV. An estimated spectral overlap of $^1/_3\,(\text{eV})^{-1}$ leads to $P_{D^* \to A^*} \sim$ 20 sec^{-1}. This value is in reasonable agreement with the experimentally determined transfer efficiency of $\sim$83% and a donor triplet lifetime of $\sim 10^{-3}$ sec.

The value of the exchange integral depends significantly on the type of orbitals used in calculations. Thus, one may estimate anywhere from 10^{-11} to 10^2 eV on going from Slater-type to Rydberg orbitals.[32] The interaction energy depends also on orientation and could conceivably vanish even at close separation distances because of spatial disposition. Vibrational distortions in the connecting frame, however, are not expected to modify the order-of-magnitude estimate, since the C–C σ bond is a rather stiff spring with a maximum amplitude in the fundamental stretching mode[36] of 0.1 Å. If anything, the norbornane–cyclopropane frame should increase the donor–acceptor orbital overlap. Whether the direct frame participation is essential for efficient exchange transfer *via* the σ bonds is difficult to estimate. Such a mechanism seems to contradict the reported lack of solvent effect in triplet–triplet energy transfer.[26] However, the analogy between separating solvent molecules and directly bonded saturated frame is not complete. Intermolecular donor–$(\text{solvent})_n$–acceptor separation distances in mixed-solutes experiments are at least twice the bonding distances in the frame. There is one additional observation which makes the frame-participation mechanism suspect. If this were the main path for triplet–triplet energy migration, there is no obvious reason why it should not take place in compound I. Since it does not, we must assume a direct exchange mechanism between the separated donor and acceptor chromophores.

Some additional contribution to the D → F triplet energy transfer should be expected to come from a resonance-type mechanism. $S_0 \leftrightarrow T_1$ transitions in unsaturated organic molecules are electric-dipole transitions which become partly allowed by mixing appropriate singlet states into the "pure" triplet states under spin–orbital interaction. The extent of Förster-type T–T transfer is only very limited for our separation distance since the R_0 value estimated from $S_0 \leftrightarrow T_1$ spectra of the D and F chromophores is less than 3 Å.

Experimental Section

General. Ir and uv spectra were determined in double beam with the Beckman Model IR5A and the Cary Model 15 spectrophotometers, respectively. Nmr spectra were recorded on a Varian A-60 spectrometer with TMS internal standard. Emission and excitation spectra were determined with an Aminco-Bowman spectrophotofluorometer. EPA solutions in the 3 mm o.d. quartz tube were lowered in the cold-finger dewar in liquid nitrogen. Elemental analysis were performed in our laboratory with an Aminco C&H analyzer. The IBM 360/40 computer was used in the calculation of the integrals.

1,4-Methano-2,3-*exo*-[fluorene-9′-spiro-3′′-1-pyrazoline]-9,10-diketo-11,12-dihydroanthracene (III). 9-Diazofluorene (5.0 g, 26.2 mmol) was dissolved in 20 ml of dry benzene containing 5.0 g (22.3 mmol) of 1,4-methano-9,10-diketo-11,12-dihydroanthracene (II). After standing at room temperature for 37 days, 4.6 g (11.0 mmol; 50%) of III was obtained as white prisms, mp 156° dec; ν^{KBr}: 1532 cm^{-1}; nmr ($CDCl_3$): δ 1.49 (2 H; C-15s,a) AB (perturbed); 1.96 (1 H; C-3) doublet (J = 6.3 cps); 3.02 (1 H; C-11) broad singlet; 3.25 (1 H; C-12) doublet (J = 4.3 cps); 3.40 (1 H; C-4) doublet (J = 5.1 cps); 3.92 (1 H; C-1) doublet (J = 5.1 cps); 5.20 (1 H; C-2) doublet (J = 6.3 cps); 6.45 (1 H; C-8′) doublet (J = 8 cps); 6.80–8.30 (11 H; aromatic) complex.

1,4-Methano-2,3-*exo*-[fluorene-9′-spiro-1′′-cyclopropane]-9,10-diketoanthracene (IV). Freshly prepared pyrazoline III (4.6 g, 11.2 mmol) was decomposed in *trans*-decalin at 160°. After 30 min the solution was cooled and 3.65 g (9.53 mmol; 85%) of light brown prisms of IV were obtained. Recrystallization from acetone yielded colorless prisms of IV, mp 205–206°; ν^{KBr} 1032 cm^{-1}; nmr (dioxane-d_8): δ 1.60 (1 H; C-15a) doublet (J = 11 cps); 1.88 (2 H; C-2,3) singlet; 1.72 (1 H; C-15a) doublet (J = 11 cps); 2.72 (2 H; C-11,12) singlet; 2.75 (2 H; C-1,4) singlet; 4.93 (1 H; C-8′) doublet (doublet) (J = 8 (0.4) cps); 5.88–7.50 (11 H; C-5–8 and 1′–7′) complex.

Anal. Calcd for $C_{28}H_{20}O_2$: C, 86.56; H, 5.19; O, 8.23; mol wt, 388. Found: C, 86.42; H, 5.08; O, 8.50; mol wt, 388M^+.

Acknowledgment. This work was supported in part by the National Aeronautics and Space Administration under Grant NGR 09-010-008.

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(36) The maximum displacement for a C–C bond was evaluated from $A = (2hc\omega/k_{\text{CC}})^{1/2}$ with $h = 6.624 \times 10^{-27}$ erg sec, $c = 3 \times 10^{10}$ cm sec^{-1}, $\omega \simeq 1000\ \text{cm}^{-1}$, and $k_{\text{CC}} \cong 5 \times 10^5$ dyn cm^{-1}. The result was $A = 0.089$ Å.