

deviations $\leq 0.2\%$).⁷ From this complex the CuOTf-*trans*-cycloheptene-*d*₄ complex was prepared photochemically.³

Copper(I) triflate-*trans*-cycloheptene-bis(*cis*-cycloheptene) complex was prepared as a colorless crystalline solid by dissolving copper(I) triflate-*trans*-cycloheptene in *cis*-cycloheptene and evaporating the solvent, followed by dissolution of the crystalline residue in hexane and evaporation to dryness. This compound was analyzed at the same day of the preparation to give the following results:

Anal. Calcd for C₂₂H₃₆CuF₃O₃S: C, 52.72; H, 7.25; Cu, 12.68; F, 11.37; S, 6.40. Found: C, 50.94; H, 6.91; Cu, 12.26; F, 11.54; S, 6.37. It easily loses cycloheptene ligands, and after 2 weeks, the analysis corresponds approximately to CuOTf-*trans*-cycloheptene-(*cis*-cycloheptene)_{0.8} (¹H NMR and elemental analysis). A CuOTf-*cis*-cycloheptene complex, having a ligand/metal ratio not exceeding 1.0, was prepared similarly.

Copper(I) triflate-*trans*-cyclooctene complex^{7a} was prepared similarly by ligand exchange. Three milliliters of *trans*-cyclooctene was refluxed with 3.5 g of (CuOTf)₂·benzene in 150 mL of hexane for 5 min, and subsequently the mixture was cooled to -20 °C. The supernatant was removed, and the remaining crystals were washed twice with 10 mL of hexane. The yield was 3.27 g (73%). NMR analysis showed that the product was free from benzene. Elemental analysis demonstrated the loss of some ligand, as was easily observable by its smell.

Anal. Calcd for C₉H₁₄CuF₃O₃S: C, 33.48; H, 4.54; Cu, 19.69; F, 17.67. Found: C, 29.02; H, 3.59; Cu, 20.50; F, 19.06.

Influence of Cycloheptene on the Cyclotrimerization in Benzene. A 58.1-mg (0.19-mmol) sample of CuOTf-*trans*-C₇ was dissolved in 2.5 mL of C₆D₆. Two 0.5-mL portions of this solution were transferred to NMR tubes, one containing 2 equiv of cycloheptene, as shown in the ¹H NMR spectrum from the 2/1 ratio of *cis*/*trans* olefinic hydrogens. With use

of *p*-xylene as an internal standard, both samples were heated to 59.5 °C for 45 min and they were analyzed afterward. The decrease of the *trans*-cycloheptene signal in the solution, containing extra cycloheptene, was approximately 50%. In the other solution the *trans* olefinic H signal had not decreased significantly. Further heating of the solutions at 70 °C for 10 min did not affect the blank solution, while in the solution, containing cycloheptene, a further 10% decrease of the *trans* signal was observed.

Cyclotrimerization of CuOTf-*trans*-C₇ in the Presence of *cis*-C₇, *trans*-C₈, or Triphenylphosphine. A solution of approximately 1 mmol of CuOTf-*trans*-C₇ was heated to 60 °C for 2 h in the presence of 4 mL of cycloolefin. The complex was destroyed afterward by pouring out the solution into 5 mL of concentrated aqueous ammonia. The ammonia layer was extracted twice with 4 mL of diethyl ether. The combined organic layers were dried with MgSO₄. Subsequently the solution was concentrated by distillation to approximately 1 mL and then analyzed on GC MS.

For the experiment with PPh₃ 0.64 mmol of CuOTf-*trans*-C₇ was dissolved in 8 mL of cycloheptene. This solution was divided into four equal portions, to which increasing amounts of PPh₃ were added (0, 1.0, 1.5, 2.0 equiv). The cyclotrimerization was performed as before. No other product than trimer **1** was found by GC MS analysis.

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Locally Excited Triplet State Production from Excited Charge-Transfer Complexes

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Abstract: The photochemistry and photophysics of a series of homologous charge-transfer complexes, involving substituted stilbenes and fumaronitrile, have been examined. The rate constants for fluorescence (k_f), production of the stilbene triplet state (k_T), and decay back to the ground state (k_d) have been determined. The values of k_T for the complexes were found to be logarithmically related to the energy gap between the initial and final states. In contrast, k_f and k_d are independent of the identity of the substituted stilbene. These results verify the previously proposed mechanism of stilbene isomerization in the parent system.

The decay of an exciplex or excited charge-transfer complex (CTC) to a locally excited triplet state has been extensively studied.¹⁻¹² Early work on excited CTC demonstrated that phosphorescence could be observed from the species with the lowest triplet energy. For example, phosphorescence from the 1,2,4,5-tetracyanobenzene/hexamethylbenzene complex is observed because the triplet state of the complex is energetically below both locally excited triplet states of the components.³ On the other hand, the triplet state of naphthalene is energetically below the triplet state of the complex formed with 1,2,4,5-tetracyanobenzene with the result that only naphthalene phosphorescence is observed.⁴

Luminescence is not the only indication of triplet state formation. Reactions typical of locally excited triplet states of either the donor or acceptor have been observed. For instance, Aloisi et al.⁵ reported that the formation of the exciplexes between styrylnaphthalene and various amines results in isomerization of the styrylnaphthalene. Similarly, Hayashi and Nagakura⁶ found

that exciplexes formed between fumaronitrile and several singlet aromatic hydrocarbons decayed with concomitant formation of maleonitrile. Both of these isomerizations have been attributed to formation of the locally excited triplet state of the acceptors.

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Recently, several mechanisms for the LE triplet state production from excited complexes have been identified. Mataga et al.⁷ have shown that in nonpolar solvents an excited complex can decay by intersystem crossing to produce an LE triplet state. In polar solvents, Weller et al.⁸ have demonstrated that triplet formation occurs from the recombination of solvated radical ions.

In order to gain further insight into the direct production of LE triplet states from excited complexes, we have investigated the photochemistry of a series of ground state complexes formed between substituted stilbenes and fumaronitrile. This system was selected for study due to several of its advantages. First, the parent system of stilbene (S)/fumaronitrile (F) has been investigated with the following results:^{9,10} (i) the complex can be selectively excited which greatly simplifies the kinetics since no back reaction (as often seen in exciplex forming systems) can occur, (ii) the excited complex has a reasonable lifetime (≈ 13 ns) and emits with a measurable quantum yield, and (iii) the excited complex decays to the S LE triplet state which results in isomerization. Another advantage is that the locally excited triplet state of stilbene is unaffected by substitution while the excited complex will be greatly affected. Consequently, it is possible to attenuate the energy gap between these two states and observe the effect on the photochemistry of the complex.

Experimental Section

Materials. *trans*-Stilbene (Aldrich) and fumaronitrile (Pfaltz and Bauer) were vacuum sublimed several times. Benzene and toluene were shaken with cold, concentrated H₂SO₄ until the acid layer remained clear, washed with bicarbonate and H₂O, dried, and fractionally distilled from CaH₂. Acetonitrile was dried over KOH and distilled from P₂O₅. Tetrabutyl ammonium perchlorate (Eastman) was dried in a vacuum desiccator over CaCl₂ for 24 h.

Synthesis of Substituted Stilbenes. The method described in ref 13 was used. The following is the procedure for the preparation of 4-methoxystilbene but the remaining stilbenes can be synthesized in an analogous manner.

Triethyl phosphite (50 mmol) and benzyl chloride (50 mmol) were gently heated for 1 h. After cooling, 10 mL of DMF was added and then sodium methoxide (50 mmol). A solution of 4-methoxybenzaldehyde (50 mmol) in DMF (40 mL) was slowly added with stirring. The temperature was maintained between 30 and 40 °C.

After standing for 12 h, the mixture was poured into 50 mL of H₂O and the crystals of 4-methoxystilbene were collected. Purification was effected by repeated recrystallization from absolute ethanol and vacuum sublimation.

Modification of the above procedure produced acceptable yields of the remaining stilbenes. However, when 4-methylbenzaldehyde was used (in the preparation of 4,4'-dimethyl- and 4,4'-chloromethylstilbene) an impurity remained even after repeated recrystallizations and vacuum sublimations. In these cases, the products were purified by preparative VPC (column: 1/4 in. \times 6 ft 5% CW 20M on Chrom W).

Spectroscopic Studies. Absorption spectra were recorded on a Bausch and Lomb Spectronic 2000. Equilibrium constants for the complexes were determined by absorption spectroscopy, using the Benesi-Hildebrand method.¹⁴

Emission spectra were recorded on an Aminco-Bowman spectrophotofluorometer. The spectra were corrected by the method of Melhuish.¹⁵ Fluorescence quantum yields of the complexes were determined relative to that of 9-bromoanthracene. The excitation wavelength was 380 nm and the absorptions of the bromoanthracene and complexes were adjusted to be equivalent in this region (<0.05).

The lifetimes of the fluorescent complexes were determined by the single photon counting method.¹⁶ In all cases, the decays were linear to at least 5 half-lives.

Isomerization Studies. a. Relative Quantum Yields. Samples of the substituted stilbenes with and without 0.2 M fumaronitrile in toluene were degassed by Ar bubbling. The concentrations of the stilbenes were adjusted so that the absorbances of the complexes at 366 nm were equivalent. These samples were irradiated on a merry-go-round apparatus, using a Hanovia 450W medium pressure Hg lamp. The 366-nm line was isolated with BiCl₃ (1 g in 150 mL of 10% HCl) and CoSO₄

Table I. Half-Wave Oxidation Potentials, Fluorescence Emission Maxima, and Equilibrium Constants for the Stilbene/Fumaronitrile Complexes

stilbene					
no.	X ₁	X ₂	E _{1/2} ^{ox} , V ^a	λ_{\max}	K, M ⁻¹
Ia	H	OCH ₃	1.17	535	0.29
Ib	CH ₃	CH ₃	1.28	521	0.29
Ic	H	CH ₃	1.37	510	0.24
Id	Cl	CH ₃	1.40	500	0.23
Ie	H	H	1.48	500	0.51 ^b
If	H	F	1.48	500	0.57
Ig	H	Cl	1.52	490	0.42
Ih	Cl	Cl	1.54	476	0.31

^a Relative to Ag|AgCl. ^b Reported as 0.17 in ref 10.

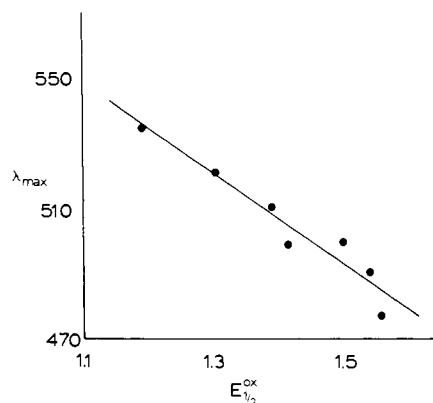


Figure 1. The linear dependence of the fluorescence maximum on the half-wave oxidation potential.

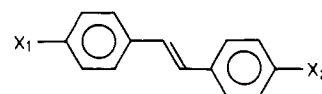
(240 g/L) filter solutions. All irradiations were carried out to less than 10% isomerization. The amount of isomerization was determined with a Varian 1440 Flame Ionization VPC equipped with a 1/8 in. \times 6 ft column containing 5% CW-20M on Chrom W.

b. Absolute Quantum Yields. The absolute quantum yield of stilbene isomerization was determined by using the same photolysis apparatus and benzophenone/benzhydrol actinometry.¹⁷ The concentrations were 0.1 M stilbene and 0.2 M fumaronitrile in toluene.

Half-Wave Oxidation Potentials. E_{1/2}^{ox} were determined with a Princeton Applied Research Model 170 electrochemical system relative to Ag|AgCl. The samples were 0.1 M in tetrabutylammonium perchlorate (acetonitrile) and 0.001 M in the stilbene.

Results

The half-wave oxidation potentials (E_{1/2}^{ox}) of the substituted stilbenes Ia-h are shown in Table I. Also shown in this table are the emission maxima of the Ia-h/F complexes. As can be seen from Table I and Figure 1, the emission maxima are linearly dependent on E_{1/2}^{ox}, as expected for complexes involving similar donors and the same acceptor.¹



- Ia, X₁ = H; X₂ = OCH₃
 b, X₁ = CH₃; X₂ = CH₃
 c, X₁ = H; X₂ = CH₃
 d, X₁ = Cl; X₂ = CH₃
 e, X₁ = H; X₂ = H
 f, X₁ = H; X₂ = F
 g, X₁ = H; X₂ = Cl
 h, X₁ = Cl; X₂ = Cl

The triplet energies of all the substituted stilbenes were determined with the aid of Saltiel plots.¹⁸ A typical example, for Ia, is shown in Figure 2. In all cases the triplet energy was found

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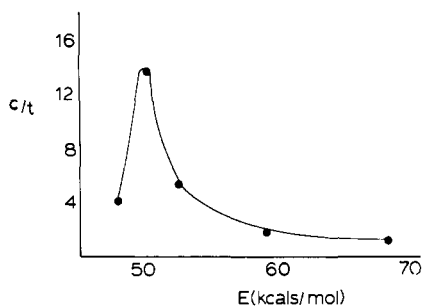


Figure 2. Saltiel plot for *p*-methoxystilbene. The triplet sensitizers were pyrene, benzil, fluorene, 2-acetylnaphthalene, and benzophenone.

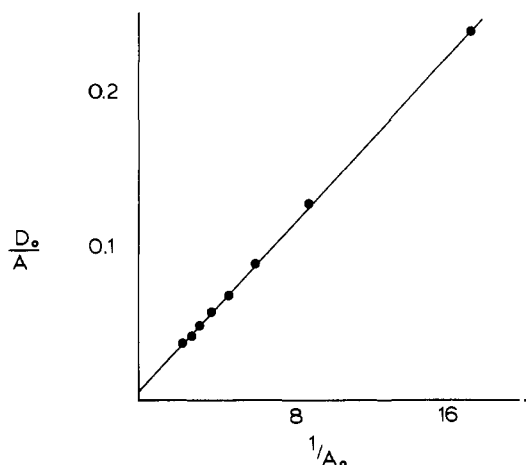


Figure 3. The Benesi-Hildebrand plot for the stilbene/fumaronitrile complex.

to be 50 ± 1 kcal/mol. This agrees with previous work on substituted stilbenes which indicated that while the singlet energy is dependent upon substitution, the triplet level is nearly unchanged.¹⁹

The equilibrium constants for the complexes were determined by the Benesi-Hildebrand method. A typical plot, for the stilbene/fumaronitrile complex in benzene is shown in Figure 3. For this complex, the equilibrium constant was evaluated as 0.51 M^{-1} . Previously, a value of 0.17 M^{-1} has been reported.¹⁰ However, such discrepancies in K values have been noted before with the conclusion that comparison of equilibrium constants determined under different conditions should be approached with caution.²⁰

The equilibrium constants for the remaining stilbenes are shown in Table I. In all cases, the values of K are in the same range, $0.6\text{--}0.2 \text{ M}^{-1}$. Interestingly, there is no apparent relationship between the donating ability of the stilbene and the equilibrium constant. Again, this has been noted and discussed previously.²⁰

When the charge-transfer band of one of these complexes is selectively excited, both isomerization of the stilbene component and fluorescence from the excited complex are observed. However, no cycloaddition products could be detected even after prolonged irradiation ($\Phi < 1 \times 10^{-3}$). The relative quantum yields of isomerization (Φ_c) were determined and are shown in Table II. These values were determined relative to stilbene and are corrected for isomerization that may occur from excitation of the stilbene itself.²¹ The absolute quantum yield for the isomerization of stilbene itself was determined as 0.11, in good agreement with the value of 0.10 reported by Lewis.⁹ The absolute quantum yields of the remaining stilbenes could then be determined and are shown in Table II.

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(21) Several of the stilbenes absorb weakly at 366 nm. Consequently, samples with and without fumaronitrile were simultaneously irradiated and the amount of isomerization determined for both. The degree of isomerization resulting from the complex could then be determined.

Table II. Relative and Absolute Quantum Yields of Isomerization and Fluorescence and the Fluorescence Lifetimes of the Stilbene/Fumaronitrile Complexes

stilbene	Φ_c		Φ_f		τ , ns
	relative	absolute	relative	absolute	
Ia	0		weak		
Ib	4.4	0.48	0.3	0.004	3
Ic	1.6	0.18	0.4	0.005 (0.006) ^a	7
Id	1.5	0.15	0.7	0.009	6
Ie	1.0	0.11	1.0	0.013 ^a	13
If	1.0	0.11	0.8	0.010	11
Ig	0.9	0.10	1.3	0.017 (0.016) ^a	11
Ih	0.8	0.09	1.4	0.018	9

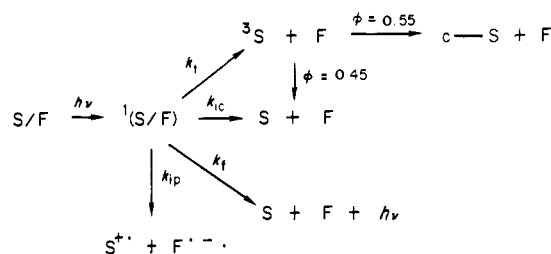
^a Values directly determined with use of 9-bromoanthracene as reference. See text.

Table III. Rate Constants (s^{-1}) for Fluorescence, Triplet Formation, and Internal Decay for the Stilbene/Fumaronitrile Complexes

stilbene	$k_f, \times 10^6$ ^a	$k_T, \times 10^6$ ^a	$k_d, \times 10^6$ ^a
Ia			
Ib	1.3 ^b	290.0 ^b	41.0 ^b
Ic	0.9	47.0	95.0
Id	1.5	46.0	119.0
Ie	1.0	15.0	60.0
If	0.9	18.0	72.0
Ig	1.5	16.0	73.0
Ih	2.0	18.0	91.0

^a $\pm 20\%$. ^b $\pm 40\%$.

Scheme I



The quantum yields of complex fluorescence were determined relative to the stilbene/fumaronitrile complex. The excitation wavelength was 380 nm and the spectra were corrected. In no case could fluorescence from the stilbene singlet state be observed. The absolute quantum yield of fluorescence from the stilbene/fumaronitrile complex was determined with use of 9-bromoanthracene as a standard. The value of 0.013 is somewhat higher than the value of 0.008 reported by Lewis and Simpson.⁹ The absolute quantum yields for the remaining complex could then be evaluated. In order to check these results, the absolute quantum yields for several other complexes (Ic, Ig) were directly determined. These values agreed with those obtained above (Table II).

The lifetimes for the fluorescent complexes were determined by time correlated single photon counting and are shown in Table II. The previously reported value of 13 ns for the stilbene/fumaronitrile complex agrees with our value. The lifetime was also found to be independent of the fumaronitrile concentration so that termolecular processes are not involved in the decay of these excited complexes. In the case of the dimethylstilbene/fumaronitrile complex, the lifetime is very short, of the order of the lamp pulse width, so that a higher error ($\pm 40\%$) is associated with it.

Discussion

The formation of triplet states from excited charge-transfer complexes or exciplexes is a well-known process. In the case of the stilbene/fumaronitrile complex, Lewis has shown that this process is indeed responsible for the stilbene isomerization.⁹ In the absence of O_2 , the proposed processes for decay of the excited complex are shown in Scheme I. The rate constants for these processes can be determined from the quantum yields of the

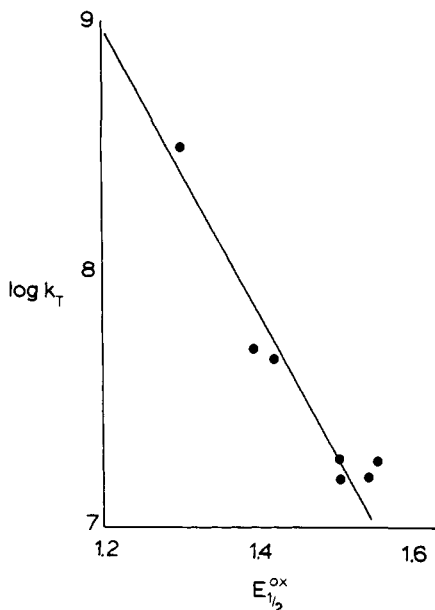


Figure 4. The linear relationship of $\log k_T$ and the half-wave oxidation potential.

individual processes and the fluorescent lifetime of the complex. These values for all of the complexes studied are shown in Table III.

The values for the rate constant of fluorescence are nearly constant ($\approx 1 \times 10^6$). Interestingly, this value agrees with those obtained for numerous exciplexes and excited CT complexes.¹¹ For example, Saltiel and co-workers determined a value of 8×10^6 for k_f in the 9,10-dichloroanthracene/2,5-dimethylhexa-2,4-diene exciplex.²² In fact, the value of k_f for excimers is also constant, within an order of magnitude of $3 \times 10^6 \text{ s}^{-1}$.²³

The values for k_T , the rate constant for intersystem crossing from the excited singlet complex to the locally excited stilbene triplet state, are expected to depend exponentially upon the energy gap between the initial and final state.²⁴ Since the triplet energies of all the stilbenes are the same ($50 \pm 1 \text{ kcal/mol}$), this energy gap will depend only on the energy of the charge-transfer state. The energy of an excited CT state is given by

$$E_{CT} = IP_D - EA_A + C \quad (1)$$

where IP_D and EA_A are the ionization potential of the donor and electron affinity of the acceptor, respectively, and C is a constant. Furthermore, since the acceptor is always fumaronitrile and the donor half-wave oxidation potential ($E_{1/2}^{ox}$) is linearly related to IP_D , eq 1 becomes eq 2, where C' incorporates the constant value of EA_A and all other constants. That eq 2 applies to the case at hand is confirmed by the linear dependence of the fluorescence λ_{max} on $E_{1/2}^{ox}$ as shown in Figure 1.

$$E_{CT} = E_{1/2}^{ox} + C' \quad (2)$$

From the above discussion, the rate constant for triplet formation (k_T) should be logarithmically related to $E_{1/2}^{ox}$. The value of k_T can be evaluated from eq 3, where Φ_c is the quantum yield

$$k_T = \Phi_c / 0.55\tau \quad (3)$$

of isomerization, τ is the fluorescence lifetime of the complex, and the 0.55 results from the fact that only 55% of the triplets yield the cis isomer.²⁵ The values obtained in this manner are shown in Table III. The value for the parent system agrees with the value of 1.4×10^7 reported by Lewis. As can be seen from Figure 4, the expected dependence of $\log k_T$ on $E_{ox}^{1/2}$ is obtained. This figure can be used to extrapolate the expected value of k_T for the *p*-methoxystilbene/fumaronitrile complex, which should be $\sim 7 \times 10^8$. The fact that no isomerization is observed indicates that the excited CT state is energetically below the triplet state.

The rate constant for decay to the ground state (k_d) is actually the sum of the rate constants for the processes of internal conversion (k_{ic}) and ion pair formation (k_{ip}). According to Scheme I, the quantum yield of internal decay is given by $1 - \Phi_F - \Phi_T$. The resulting values are shown in Table III. Like the values for k_f , the values for k_d are clustered around a single value, 9×10^7 . The consistency of these rate constants probably results from the fact that the energy gap between the initial (excited CT) state and final (ground CT) state is so large that the small changes brought about by substitution represent a small change in this energy.

As mentioned previously, the fact that no isomerization results from irradiation of the *p*-methoxystilbene/fumaronitrile complex indicates that production of the triplet state is an endothermic process. If the consistency of k_f ($\approx 1 \times 10^6$) and k_d ($\approx 9 \times 10^7$) is assumed, then there should be a high yield of fluorescence ($\sim 1\%$). However, the fluorescence from this complex is so weak that it is difficult to quantitate. The fluorescence quantum yield can be estimated as approximately 1×10^{-3} . This requires the value of k_d to be $\geq 1 \times 10^9$. This sudden increase in k_d is due to the opening of a new reaction channel for the excited complex. For the complexes involving Ib-h, the major contributor to k_d is apparently k_{ic} and ion pair formation is unlikely. On the other hand, the sudden increase in k_d for Ia results from the increased feasibility of forming ion pairs. It should be noted that the lack of both fluorescence and isomerization cannot be rationalized by ion pair formation since the expected rate constant for triplet formation is 7×10^8 . This process should then be able to compete with ion pair formation.

Conclusion

The photochemistry and photophysics of a homologous series of charge-transfer complexes, involving substituted stilbenes and fumaronitrile, have been examined. The previously proposed mechanism of stilbene isomerization was decay from the excited complex to the locally excited triplet state of the stilbene component. Our results support this mechanism. The lack of isomerization in one case, *p*-methoxystilbene, can be attributed to the fact that the *CT is energetically below the locally excited triplet state. The lack of fluorescence is possibly due to the formation of ion pairs.

Interestingly, the radiationless decay from the excited CT state to the LE triplet state appears to be quite similar to radiationless processes in uncomplexed molecules. The rate constants for this process in a series of complexes are logarithmically related to the energy gap separating the initial and final states.

Acknowledgment. This work was supported by grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the National Science Foundation (No. ISP-8011453).

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