

Photochemistry of the Phenanthrene-Stilbene System. Cycloaddition and Singlet-Sensitized Isomerization[†]

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Abstract: Photocycloaddition of phenanthrenes to stilbenes is a general and remarkably facile reaction. Two isomeric trans adducts often result with unsymmetrical phenanthrenes. The product with *cis*-stilbene and 9-cyanophenanthrene is the crowded *cis*, *endo* isomer. With 9-cyanophenanthrene and *trans*-stilbene, geometric isomerization occurs but only in a triplet process. With *cis*-stilbene, geometric isomerization results from the triplet, and both geometric and valence isomerizations can be induced by singlet 9-cyanophenanthrene. The reactivity of the stilbene isomers can be accounted for by an algorithm we have previously derived, as can the 20- to 30-fold enhancement of stilbenes over styrenes as a reactant in cycloadditions to phenanthrene. The possibility of singlet-sensitized valence isomerization as a mechanism for storage of solar energy is discussed.

Starting with the pioneering work of Hammond et al., the stilbene isomers have proved valuable models for studying a rich variety of photoreactions. Much of our knowledge of triplet¹ and singlet² state olefin geometric isomerizations derives from work with these compounds. The valence isomerization of *cis*-stilbene to 4a,4b-dihydrophenanthrene has been studied extensively,³ as have bimolecular photocycloadditions⁴ and photochemical electron-transfer reactions involving stilbene and stilbene derivatives.⁴

Recently, we have presented an algorithm⁵ which allows rough estimation of reactivity in allowed, singlet state photocycloadditions. Applied to the phenanthrene-stilbene system, it afforded the predictions that *trans*-stilbene would be an extremely reactive addend for the phenanthrene chromophore and *cis*-stilbene a moderately reactive one. We had previously noted, qualitatively, that the former appeared likely. The genesis of the present work was the confirmation of that preliminary conclusion and the exploration of the potential of *cis*-stilbene as an addend. Our results show that both stilbene isomers behave essentially as predicted, thus giving further credence to our algorithm. We have also examined the effect of charge-transfer (CT) inducing substituents. Finally, in the course of this work, we have noted singlet-sensitized geometric and valence isomerizations of *cis*-stilbene and have reached a conclusion as to the probable mechanism.

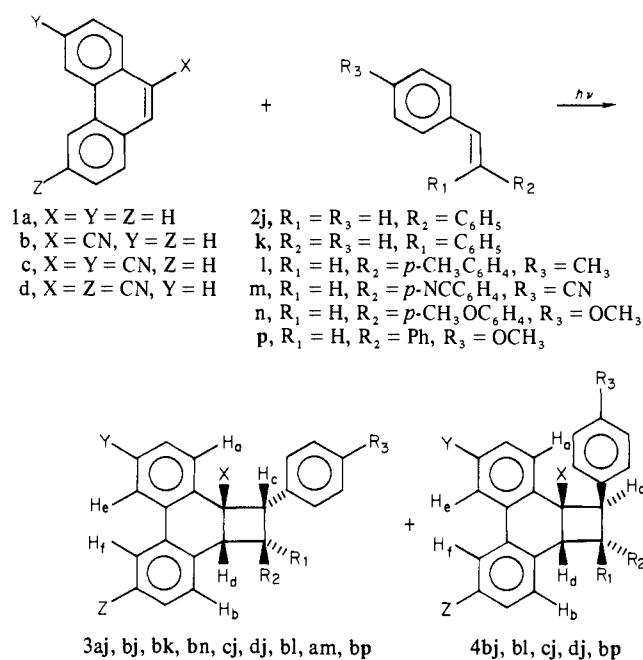
Experimental Section

Materials. The preparations of 3,9-dicyanophenanthrene,⁶ 3,10-dicyanophenanthrene,⁶ 4,4'-dicyanostilbene,⁷ 4-methoxystilbene,⁸ and 4,4'-dimethylstilbene⁸ followed established procedures. Phenanthrene and benzene were purified as previously described.⁹ Azulene (Aldrich) was doubly sublimed. *trans*-Stilbene was recrystallized from ethanol; *cis*-stilbene obtained from Aldrich chemical Co. was found to contain <0.14% of *trans* impurity and was chromatographed on alumina and then vacuum distilled. In some experiments, *cis*-stilbene was used which was isolated from sensitized photoisomerization of *trans*-stilbene (benzil sensitizer), chromatographed, vacuum distilled, and fractionally frozen at ca. -5 °C to enrich the supernatant. This afforded material containing 0.9% *trans*, which proved adequate for qualitative studies or for photoisomerizations (see text) in which conversion to *trans* was high.

Irradiations were generally performed in benzene under nitrogen using a Corning 3320 filter sleeve. In most cases the major photoadduct could be obtained pure by concentration of the reaction mixture, collection of the crystals, and one more recrystallization from benzene or benzene-ethanol. Isolation of the minor product **4bj** from the reaction of 9-cyanophenanthrene and *trans*-stilbene required repetitive recrystallization from the mother liquor. Isolation of the 9-cyanophenanthrene-*cis*-stilbene adduct **3bk** required careful column chromatography on silica gel using benzene-hexane eluent. Table I describes the adducts, and Table II lists microanalysis results (MHW laboratories).

Fluorescence spectra and Stern-Volmer experiments were performed with a Farrand MK-1 spectrofluorimeter at ambient temperature (24 °C).

Scheme I



Quantum yields were performed as described previously⁹ by using one or two Bausch and Lomb SP-200 monochromators, to isolate the 365-nm regions of the mercury lamp, and a rotating sample stage. Care was taken to ensure that the exciting light was absorbed only by the phenanthrene. Samples in benzene were subjected to three or four freeze-pump-thaw cycles and sealed under vacuum (<10⁻⁴ torr) in 13-mm Pyrex ampules. Ferrioxalate actinometry was generally employed, although occasionally the benzophenone-sensitized isomerization of *trans*-stilbene¹⁰ proved convenient.

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[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

Table I. Properties of Adducts

adduct	mp, °C	% yield	chem shift, ppm from Me ₄ Si in CDCl ₃							recrystallization solvent		
			H _a	H _b	H _c	H _d	R ₁	R ₂	R ₃		H _e , H _f	
3aj	183.5–184.5	55	6.2		3.9	4.25	4.05 ^a				7.95	C ₆ H ₆ -EtOH
3bj	227.5–228.5	65	6.35		4.08	4.58	3.80 ^a				7.9	C ₆ H ₆
3bk	157–160	25			4.6	5.19			4.6 ^a		7.7	C ₆ H ₆ -EtOH
3bl	185.5–186.5	45	6.35		4.00	4.50	3.70 ^a			2.28 ^b	7.9	C ₆ H ₆ -EtOH
3cj	205–205.5	73	6.40		4.10	4.65	3.75 ^a				7.8	C ₆ H ₆
3dj	181–182	81	6.40		4.15	4.65	3.80 ^a				7.9	C ₆ H ₆ -EtOH
3bn	202–204.5	24	6.35		3.85	4.65				3.75 ^d	7.9	MeOH
3am	194–200	62	6.1		<i>e</i>	<i>e</i>	<i>e</i>				7.9	C ₆ H ₆ -hexane
3bp	139–141	85	6.37		4.08	4.55	<i>f</i>			3.76 ^d	8.0	EtOH
4bj	190.5–191.5	15		6.17	4.2	4.45	4.9 ^a				7.9	EtOH
4bp	209–211	5		6.14	4.10	4.45	4.88 ^a			3.72 ^d	7.9	C ₆ H ₆ -EtOH
4bl	<i>c</i>	<i>c</i>		6.15	4.2	4.35	4.8 ^a			2.28 ^b
4cj	<i>c</i>	<i>c</i>								
4dj	<i>c</i>	<i>c</i>								

^a Methine hydrogen. ^b Methyl hydrogen. ^c Detected in crude product by NMR but not isolated. ^d Methoxy group. ^e Multiplets of equal intensity centered at δ 3.85 and 4.3. No further assignment is made. ^f Obscured by methoxy group at δ 3.76.

Table II. Analyses of Adducts

adduct	calcd			found		
	C	H	N	C	H	N
3aj	93.81	6.19		94.01	5.99	
3bj	90.83	5.52	3.65	90.95	5.53	3.64
3bk	90.83	5.52	3.65	90.61	5.59	3.58
3bl	90.47	6.12	3.40	90.53	6.08	3.39
3cj	88.21	4.93	6.86	88.45	4.84	6.90
3dj	88.21	4.93	6.86	88.40	5.06	6.85
3bn	83.97	5.64		84.01	5.82	
3am	88.21	4.93	6.86	88.44	4.94	6.82
3bp	87.14	5.61	3.39	87.29	5.66	3.44
4bj	90.83	5.52	3.65	90.77	5.33	3.68
4bp	87.14	5.61	3.39	87.73	5.45	3.40

Analyses of stilbene isomers were performed by gas chromatography on a short column on which pyrolysis of adducts was negligible. Analyses of adducts were performed by HPLC on a Waters ALC-202 instrument using hexane-chloroform as solvent. In most experiments, even though a Corasil I and a Corasil II column were coupled, only partial separation of **3bj** and **4bj** resulted. Complete separation was effected in some experiments on a Microporasil column. Internal standard for trans-cis isomerization (GC) was tetradecane and for cycloaddition (HPLC) was phenyl benzyl ketone; each was added after irradiation.

Conversions to cycloadduct were low (ca. 1%), as were conversions to the appropriate geometric isomer in general. At low concentrations ($<5 \times 10^{-3}$ M) of *cis*- or *trans*-stilbene, quantum yields for cycloaddition were small, and larger conversions (5–10%, and in one case 20%) to the geometric isomer were accepted as a necessity if cycloadduct were to be detected. All isomerization yields, including benzophenone-*trans*-stilbene actinometry, were corrected by the method of Lamola and Hammond.¹¹ Any errors so introduced would be significant only at the triplet reaction limit of the stilbene and thus have no bearing on the singlet chemistry. In fact (see Discussion), ϕ_{isc} as measured for 9-cyanophenanthrene compares well to a previous independent determination, leading us to believe that there are no significant errors even at low stilbene concentrations.

Results

Cycloadditions. Scheme I summarizes the cycloadditions observed.

Structure assignments for the various products follow analogously to those previously reported⁶ for the β -methylstyrene series. The *trans*-aryl nature of all adducts (except **3bk**) isolated follows from their pyrolysis upon gas chromatography with injector temperature of 350 °C. These compounds all afforded the *trans*-stilbene with $\leq 2\%$ of *cis*-stilbene. For **3bk**, the *cis*-phenyl structure assigned was confirmed by similar pyrolysis, which afforded an 85:15 ($\pm 2\%$) ratio of *cis*- to *trans*-stilbene.

The NMR spectra in the benzylic region in the **3** series were quite similar. The **4** series was also internally similar but was readily distinguished from the **3** series. Assignment of the upfield aromatic hydrogen in the **3** series as H_a follows from its appearance

Table III. Effect of Sensitizer and Quencher on the Photocycloaddition of *trans*-Stilbene to 9-Cyanophenanthrene

condtns ^a	% of cycloadduct	<i>cis</i> -stilbene ^c
<i>a</i>	64	68
0.2 M isoprene	76	45
1.0 M isoprene	78	26
7.5×10^{-4} M MK ^d	<5	57
5×10^{-3} M MK ^d	<5	62
0.1 M <i>trans</i> -stilbene	>95	6

^a (9-Cyanophenanthrene) = 0.02 M, (*trans*-stilbene) = 0.02 M, 75 min under N₂ through Corning 3320 filter except as noted.

^b Calculated from the NMR spectrum of the reaction mixture.

^c Percent of remaining total stilbene. ^d Michler's ketone.

as a simple doublet, showing only ortho coupling, in **3cj**, but with the peaks broadened in **3dj** by the added meta coupling. The **4** series of structures thus follows as the alternative *trans* adducts.

The *cis*-phenyl adduct **3bk**, only obtained in significant yield from *cis*-stilbene, appears to have endo phenyl groups, i.e., *cis* to the biphenyl moiety. The cyclobutane hydrogens are at lower field in the NMR than for the *trans* adducts, and H_e and H_f, the lowest field aryl hydrogens, are centered at δ 7.78, contrasting with δ 7.8–7.95 for the *trans* adducts (Table I). The aromatic ring current effects induced by the endo phenyls are expected to cause the latter, while the absence of a ring current effect on the *exo* side accounts for the former.

The *trans* structures for the phenanthrene-stilbene and phenanthrene-dicyanostilbene adducts follow clearly from the relatively complex pattern for the benzylic hydrogens. Either *cis* adduct in these cases would have shown a symmetric A₂B₂ spectrum.

The assignments of **3bp** as a type **3** adduct and **4bp** as a type **4** are clear from the NMR spectra, but the assignment of *exo* aryl vs. *exo* phenyl in each is only tentative.

Multiplicity. The cycloadditions of phenanthrene and 9-cyanophenanthrene with *trans*-stilbene are strongly quenched by the addition of Michler's ketone, the only reaction observed being *cis*-*trans* isomerization of the stilbene. As shown in Table III, addition of the triplet quencher isoprene in fact increases the rate of formation of *trans* cycloadducts from 9-cyanophenanthrene and *trans*-stilbene at constant irradiation time, presumably by attenuating isomerization to *cis*-stilbene. A high concentration of *trans*-stilbene quenches nearly all 9-cyanophenanthrene fluorescence, sharply inhibits geometric isomerization, and causes a further increase in adduct formation rate. All these observations suggest that isomerization is a triplet state reaction, while cycloaddition is a singlet state reaction, for 9-cyanophenanthrene and *trans*-stilbene.

The quantum yield of formation of the 9-cyanophenanthrene-*cis*-stilbene adduct is low but is substantially higher at high *cis*-stilbene concentrations. The result also suggests singlet multiplicity for this cycloaddition, since the increase roughly

(11) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.

Table IV. Quenching of Fluorescence of the Phenanthrenes by the Stilbene Isomers

phenanthrene	<i>trans</i> -stilbene		<i>cis</i> -stilbene	
	k_{QT}, M^{-1}	$k_Q, M^{-1} s^{-1}$	k_{QT}, M^{-1}	$k_Q, M^{-1} s^{-1}$
unsubstituted	2.0	1.0×10^8		
9-cyano	48.8 (66.4)	3.2×10^9	26.6	1.7×10^9
3,9-dicyano	91.7 (122.1)	9.8×10^9	46.8	5.0×10^9
3,10-dicyano	81.6 (129.6)	7.2×10^9	38.3	3.4×10^9
3,6-dimethoxy	6.0		10.1	
3-methoxy-9-cyano	21.6	1.8×10^9	12.4	1.0×10^9
3-methoxy-10-cyano	20.0	1.0×10^9	7.3	3.7×10^8

^a In air; values in parentheses are under nitrogen.

Table V. Properties of Exciplexes between Phenanthrenes and the Stilbene Isomers^a

phenanthrene	<i>trans</i> -stilbene		<i>cis</i> -stilbene	
	λ_{max}, nm	τ, ns^b	λ_{max}, nm	τ, ns^b
9-cyano	not observed		not observed	
3,10-dicyano	445	4.6	440	2.3
3,9-dicyano	460	20	450	2.7

^a In benzene. ^b By aerated vs. outgassed intensity ratios; see: Caldwell, R. A.; Creed, D.; DeMarco, D. C.; Melton, L. A.; Ohta, H.; Wine, P. H., *J. Am. Chem. Soc.* 1980, 102, 2369.

correlates with the quenching of 9-cyanophenanthrene fluorescence.

We have not checked the other reactions reported but believe all cycloadditions to be singlet reactions by analogy to the above.

Fluorescence Quenching. Exciplex Emissions. Tables IV and V give the Stern-Volmer slopes, the phenomenological fluorescence quenching rates (derived from the previously reported lifetimes⁶), and the properties of exciplexes when detected. In general, quenching rates approach the diffusion-controlled limit and exciplex fluorescence is most intense when good donor-acceptor interactions are expected. In these respects, the results are unexceptional. Two interesting differences with our previous study of phenanthrenes and styrenes were noted, however. First, the exciplex emissions are generally relatively weak, and the lifetimes short, compared to the corresponding phenanthrene- β -methylstyrene series. Second, although the effect of steric hindrance was to diminish reactivity with the styrenes,¹² thus increasing exciplex fluorescence, the quenching of 9-cyanophenanthrene by *cis*-stilbene was more rapid than we expected and exciplex fluorescence was absent. The exciplex that would be precursor to the *cis* adduct **3bk** would be quite hindered. These results suggested high reactivity for both the *trans*- and *cis*-stilbene exciplexes, and we wished to define its origins. A quantitative study of the photoreactions of 9-cyanophenanthrene with the stilbene isomers defined the source of the high reactivity in each case; interestingly, the major processes are entirely different.

Quantum Yields from *trans*-Stilbene. Table VI and Figure 1 summarize results for *trans*-stilbene and 9-cyanophenanthrene. When plotted as a function of fractional 9-cyanophenanthrene fluorescence quenching f , they show that isomerization is maximized at low f and is negligible when $f = 1$. Obviously isomerization to *cis* requires a triplet process and is excluded in the singlet. By contrast, cycloadduct formation is maximized by high f , pointing to a singlet mechanism with no significant triplet component. The high extrapolated value for the quantum yield of cycloadducts ($\phi = 0.66$) points to a very efficient process. The energy wastage quantum yield $0.34 (= 1 - 0.66)$ presumably can be ascribed to partitioning at pericyclic minima, its magnitude being quite reasonable compared to that obtained in the cyanophenanthrene- β -methylstyrene series.^{13,14} Clearly, the high re-

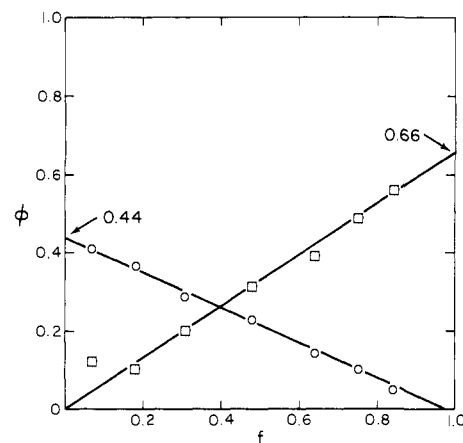


Figure 1. Quantum yields of cycloaddition (\square) and *trans*-*cis* isomerization (\circ) of *trans*-stilbene as a function of the fractional quenching f of the fluorescence of 9-cyanophenanthrene.

Table VI. Quantum Yields of Isomerization and Cycloaddition with *trans*-Stilbene and 9-Cyanophenanthrene^a

<i>trans</i> -stilbene, M	$f = 1 - F/F_0^b$	$\phi_{t \rightarrow c}$	$\phi_{cycloadduct}$
1.4×10^{-3}	0.07	0.41 ^c	0.12
3.1×10^{-3}	0.18	0.37	0.10
6.7×10^{-3}	0.31	0.29	0.20
1.25×10^{-2}	0.48	0.23	0.31
2.33×10^{-2}	0.64	0.14	0.39
3.78×10^{-2}	0.75	0.10	0.49
7.11×10^{-2}	0.84	0.05	0.56

^a (9-cyanophenanthrene) = 0.05 M in degassed benzene. ^b $F =$ fluorescence intensity of 9-cyanophenanthrene. Accordingly, f is the fractional quenching of 9-cyanophenanthrene fluorescence by *trans*-stilbene at the stated concentration. ^c Corrected by the method of: Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* 1965, 43, 2129.

activity of the 9-cyanophenanthrene-*trans*-stilbene exciplex is ascribable to very high propensity toward photocycloaddition.

We have conducted a similar study with air-saturated solutions. The extrapolated cycloaddition quantum yield is the same as for the degassed experiments. This requires an exciplex so short-lived that it is not quenched by O_2 at this concentration, again consistent with high reactivity. The quantum yield for isomerization to *cis*-stilbene extrapolated to $f = 0$ is higher ($\phi = 0.48_0$) when compared to the degassed value ($\phi = 0.44_2$). Comparison with the value of 0.56 for the benzophenone ($\phi_{isc} = 1.00$) sensitized of *trans*- to *cis*-stilbene isomerization¹⁰ affords ϕ_{isc} values of 0.79 degassed and 0.86 air saturated for 9-cyanophenanthrene. The enhancement of intersystem crossing by 3O_2 is consistent with previous studies;¹⁵ in the present case, we estimate that $95 \pm 15\%$ of the encounters of singlet 9-cyanophenanthrene with 3O_2 result in triplet 9-cyanophenanthrene.

The degassed value of 0.79 for ϕ_{isc} of 9-cyanophenanthrene is acceptably close to the value of 0.84 determined by *trans*-anethole geometric isomerization.¹⁶ Since the present ϕ_{isc} determination is sensitive to any error introduced by the relatively large conversions to the geometric isomer at low stilbene concentration (see Experimental Section), the agreement with an independent determination is good confirmation that the present quantum yields are accurate.

Quantum Yields from *cis*-Stilbene. *cis*-Stilbene is a less efficient quencher for 9-cyanophenanthrene singlet than *trans*, and under all conditions (Figure 2) *cis*-*trans* isomerization is very rapid. It proved difficult to study the cycloaddition of *cis*-stilbene to 9-cyanophenanthrene quantitatively because of the rapid buildup of *trans*-stilbene as a quencher for the cycloaddition of *cis* and

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(13) Caldwell, R. A.; Creed, D. *J. Am. Chem. Soc.* 1978, 100, 2905.

(14) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* 1980, 13, 45.

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(16) Creed, D., unpublished data. Maw, T. S. M.S. Thesis, University of Texas at Dallas, 1977, Table III, p 52.

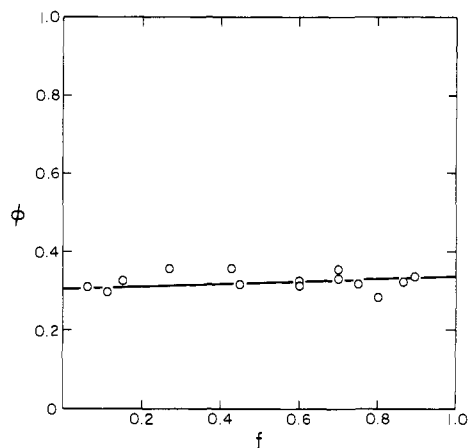


Figure 2. Quantum yield of isomerization of *cis*-stilbene to *trans*-stilbene as a function of the fractional quenching of *f* of 9-cyanophenanthrene fluorescence.

Table VII. Formation of Cycloadducts from 9-Cyanophenanthrene and *cis*-Stilbene^a

<i>cis</i> -stilbene, M	<i>f</i>	relative yield of 3bk to 3bj		
		ϕ_{3bk}	ϕ_{3bj}	
0.028	0.43	0.48	0.0025	0.005
0.056	0.60	0.61		
0.112	0.75	1.27		
0.28	0.88	2.59	0.030	0.012
0.50	0.93	2.80	0.038	0.013

^a 9-Cyanophenanthrene, 0.05 M, irradiation at 365 nm for 7 h.

the relatively low quantum yield of the cycloaddition. Table VII shows that the quantum yield of *cis* cycloadduct (**3bk**) formation is higher at high *f*, consistent with a singlet reaction, but the reaction cannot be further dissected quantitatively.

We note that the ratio of *trans* adducts **3bj** and **4bj** is the same starting from *cis*-stilbene as from *trans*-stilbene. It seems unlikely that this could arise, except fortuitously, from biradical intermediates. We therefore believe that the *trans* adducts we observe in the reaction starting with *cis*-stilbene are secondary products arising from *trans*-stilbene produced by isomerization. The quantum yields of formation are acceptably in accord with the fraction of *trans*-stilbene present and with the relative quenching efficiencies of *trans*- and *cis*-stilbenes for 9-cyanophenanthrene singlet.

The *cis*-endo adduct **3bk** is therefore the dominant, if not exclusive, cycloadduct arising from *cis*-stilbene, with a quantum yield in excess of 0.04 but probably not significantly greater than 0.05. We have noted a fourth peak in the HPLC of reactions starting with *cis*-stilbene, in the adduct region, which might be the remaining *cis*-exo adduct. It is formed in a yield ca. 5% of that of **3bk** and has not been isolated.

The Major Singlet Process from 9-Cyanophenanthrene and *cis*-Stilbene. Clearly, cycloaddition is not the major singlet path in this case as it is with *trans*-stilbene and 9-cyanophenanthrene although, with ϕ of ca. 0.05, it is certainly not insignificant. Geometric isomerization to *trans*-stilbene dominates. Our initial thought was that this was due to anomalously efficient intersystem crossing in a singlet exciplex between 9-cyanophenanthrene and *cis*-stilbene. The azulene effect^{1,2} is diagnostic for the presence of triplet stilbene, since its ability to quench triplet stilbene exclusively to *trans*¹ enhances the quantum yield of isomerization in a triplet mechanism. We accordingly studied the effect of azulene on the quantum yield of *trans*-stilbene from *cis*-stilbene at high *f*. As will be shown, the results preclude significant intersystem crossing.

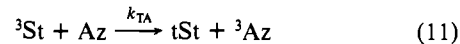
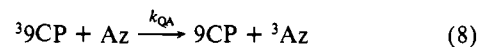
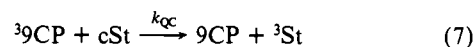
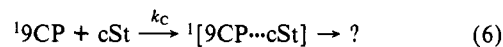
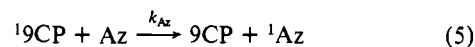
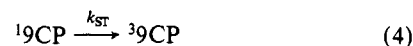
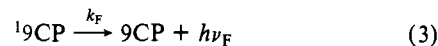
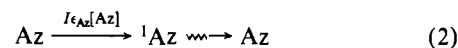
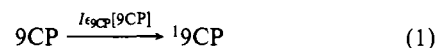
In Table VIII, the quantum yields of *trans*-stilbene, $\phi_{c \rightarrow t}$, are seen to decrease as the azulene concentration increases. A variety of processes can quench the process, however, and must be considered before the effect of azulene on this isomerization resulting exclusively from the singlet interaction can be calculated. Consider

Table VIII. Effect of Azulene on the Quantum Yield of Formation of *trans*-Stilbene from *cis*-Stilbene on Singlet Sensitization by 9-Cyanophenanthrene^a

azulene, M	$\phi_{c \rightarrow t}$	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	$\phi_{Ex \rightarrow tSt}$
0	0.334	1	0.868	0.105	1	0.45	0.33 ₁
2×10^{-3}	0.307	0.976	0.794	0.0954	0.977	0.519	0.33 ₆
4×10^{-3}	0.265	0.953	0.730	0.0878	0.955	0.572	0.31 ₅
6×10^{-3}	0.242	0.931	0.676	0.0813	0.934	0.615	0.31 ₅
8×10^{-3}	0.233	0.910	0.630	0.0757	0.914	0.650	0.33 ₅
1×10^{-2}	0.205	0.890	0.589	0.0708	0.894	0.679	0.31 ₇

^a (9-Cyanophenanthrene) = 0.05 M; (*cis*-stilbene) = 0.254 M.

the following mechanism, where 9CP = 9-cyanophenanthrene, Az = azulene, tSt = *trans*-stilbene, and cSt = *cis*-stilbene.



This mechanism affords eq 12

$$\phi_{c \rightarrow t} = B(C\phi_{Ex \rightarrow tSt} + DEF) \quad (12)$$

where $B = \epsilon_{9CP}[9CP]/(\epsilon_{9CP}[9CP] + \epsilon_{Az}[Az])$ (competitive absorption of light), $C = k_C[cSt]/(k_C[cSt] + k_{Az}[Az] + k_F + k_{ST})$ (probability of quenching 19CP by cSt), $\phi_{Ex \rightarrow tSt}$ = probability of formation of tSt as a result of quenching of 19CP by cSt, $D = k_{ST}/(k_C[cSt] + k_{Az}[Az] + k_F + k_{ST})$ (isc of 19CP), $E = k_{QC}[cSt]/(k_{QC}[cSt] + k_{QA}[Az])$ (probability of forming 3St from 39CP), and $F = (k_{DT} + k_{TA}[Az])/(k_{DT} + k_{DC} + k_{TA}[Az])$ (probability of ${}^3St \rightarrow tSt$).

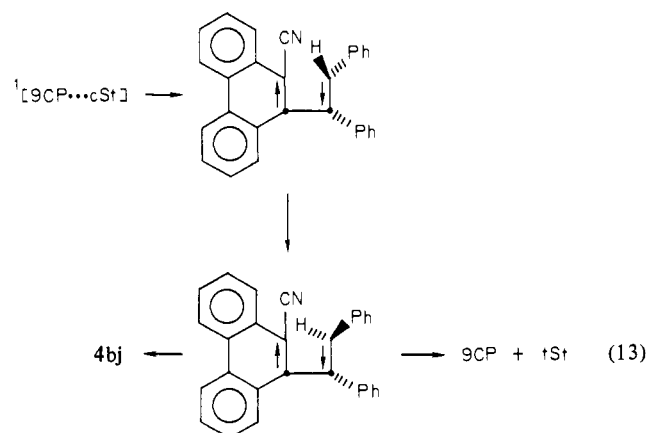
Values of *B*, *C*, *D*, *E*, and *F* were determined from the relevant extinction coefficients and kinetic parameters. They are tabulated in Table VIII. Extinction coefficients of 9CP and Az at 366 nm were measured as 34 and 21 M⁻¹ cm⁻¹, respectively. Singlet quenching parameters were obtained straightforwardly from the Stern-Volmer slopes; a correction for Az absorption was necessary. The value of $k_{ST} = 0.79 (k_F + k_{ST})$ follows from ϕ_{isc} (degassed) above. Values of $k_{QC} = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{QA} = 6.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ were determined directly by kinetic absorption spectrophotometry. Values of $k_{TA}/k_{DT} = 130 \text{ M}^{-1}$ and $k_{DT}/k_{DC} = 0.68$ follow from Hammond's studies of triplet stilbene.¹

Errors in *B*, *C*, *D*, *E*, and *F* must be considered carefully in order to assess the validity of conclusions drawn from $\phi_{Ex \rightarrow tSt}$. For *D*, *E*, and *F*, eq 12 makes it clear that even rather large errors could be tolerated. Note that *DEF* (the overall probability of the triplet route ${}^19CP \rightarrow {}^39CP \rightarrow {}^3St \rightarrow tSt$) is only ca. 20–25% of the value of $C\phi_{Ex \rightarrow tSt}$; the expected $\pm 10\%$ errors in rate constants and $\pm 5\%$ errors in steady-state-derived parameters will thus introduce only ca. 2–3% error in $\phi_{Ex \rightarrow tSt}$, and much less in its dependence on [Az]. The value of *B* could be subject to systematic errors because of the substantial (ca. 9-nm) excitation width, a combination of the 9.6-nm slit width and a lamp profile that peaks at the 366-nm mercury line. Careful and repetitive extinction coefficient de-

termination and integration of B over reasonable overall slit/lamp combination profiles afforded the following deviations at 0.05 M 9CP and 0.01 M (the maximum) Az: 0 nm, 0%; 6 nm, 1.5%; 12 nm, 3%. We anticipate a maximum of 2% error in B . For C , an error in k_c will essentially only change the magnitude of $\phi_{\text{Ex} \rightarrow \text{St}}$, while an error in k_{Az} will change its dependence on $[\text{Az}]$. A 10% error in the latter will cause a ca. 3% error in C . Altogether, these error estimates suggest that $\phi_{\text{Ex} \rightarrow \text{St}}$ is precise to about $\pm 6\%$, when a ca. 3% precision limit to the experimental quantum yield is included.

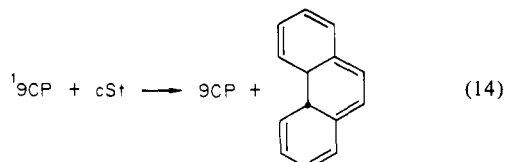
Since $\phi_{\text{Ex} \rightarrow \text{St}}$ is constant at 0.325 ± 0.010 , no significant production of ^3St results from the quenching of $^1\text{9CP}$ by cSt . The several triplet possibilities, e.g., intersystem crossing of a putative $^1[\text{9CP} \cdots \text{cSt}]$ exciplex or electron transfer followed by isc and recombination, are ruled out, since $\phi_{\text{Ex} \rightarrow \text{St}}$ should have increased substantially in the presence of Az. The magnitude of the effect would have been the same as on F , which increases more than 50% in the range of $[\text{Az}]$ studied. The 6% precision limit for $\phi_{\text{Ex} \rightarrow \text{St}}$ sets an upper limit of about 12% for an isc contribution to the isomerization.

If isc is not the mechanism responsible for geometric isomerization, what is? One hypothesis is formation of a singlet biradical, bond rotation, and scission (eq 13). We cannot rigorously



eliminate this possibility, although we feel there is a better explanation (vide infra). There is a circumstantial argument against it from the invariance of the trans adduct ratio in the cycloaddition starting from *cis*-stilbene. If a biradical intervenes in the isomerization, we believe it will likely also intervene in the cycloaddition. The biradical depicted in (13), because of the stabilizing effect of the cyano group, should predominate over its regioisomer with collapse at the 9-position of 9CP and the cyano thus deconjugated. The expected biradical can lead only to the minor trans adduct or to the *cis* adduct, and the absence of enhanced yields of minor trans adduct thus argues against the biradical.

Valence Isomerization of *cis*-Stilbene Sensitized by Singlet 9-Cyanophenanthrene. Evidence for Singlet Excitation Transfer. The key to the dominant exit channel from $^1[\text{9CP} \cdots \text{cSt}]$ was provided by the observation that a yellow color formed rapidly during the irradiation and bleached over a period of hours. The yellow color showed a λ_{max} at 450 nm and disappeared with first-order kinetics ($k_1 = 8.2 \times 10^{-3} \text{ min}^{-1}$ in benzene at room temperature). These results are strikingly similar to the behavior³ of the known 4a,4b-dihydrophenanthrene formed upon direct photochemical valence isomerization of *cis*-stilbene, and we assign the source of the yellow color as eq 14.



To rule out the possibility of direct isomerization by competitive absorption of the 366-nm exciting light by cSt , we studied the

Table IX. Dihydrophenanthrene Formation in the Presence of 9-Cyanophenanthrene in Benzene^a

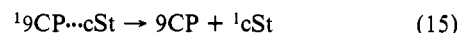
9-cyano-phenanthrene, M	OD _{max} ⁴⁵⁰ b	time to reach photostationary state
3×10^{-3}	0.05	~10 min.
3×10^{-3}	0.10	~8 min.
1×10^{-2}	0.18	~8 min.
5×10^{-2}	0.47	~40 min.

^a (*cis*-Stilbene) = 0.11 M. Irradiation of nitrogen-purged samples at 365 nm. ^b Optical density observed at 450 nm at photostationary state.

formation of 4a,4b-dihydrophenanthrene as a function of 9CP concentration. The photostationary yield is higher at all finite values of $[\text{9CP}]$ than in the absence of 9CP (Table IX), clearly showing the sensitized nature of the preponderance of the valence isomerization.

We at first (incorrectly) suspected that charge transfer and exciplex formation were important in the valence isomerization. If CT were important, we expected enhancement in polar solvents. We noted that the photostationary yield of dihydrophenanthrene was lower in ethyl acetate ($3.7 \times 10^{-5} \text{ M}$) vs. benzene ($6.5 \times 10^{-5} \text{ M}$) and that it was not formed in detectable amounts in acetonitrile. Quantum yields in benzene (0.017) and ethyl acetate (0.020) were similar. Neither result suggests that CT is important to the valence isomerization.

Comparison of the sensitized quantum yields we obtain with literature values for geometric isomerization ($\phi_{\text{c} \rightarrow \text{t}} = 0.35^2$) and valence isomerization ($\phi < 0.1$)³ of *cis*-stilbene on direct irradiation is revealing. Our sensitized values of 0.32₅ and 0.02, respectively, are strikingly similar. It seems very likely, therefore, that the majority of $^1[\text{9CP} \cdots \text{cSt}]$ exciplexes (or singlet quenching encounters, since we have no definitive evidence for exciplex formation) simply decay via singlet excitation transfer.



With the assumption of this mechanism, the geometric isomerization sensitized/direct quantum yield ratio affords an estimate of the excitation transfer efficiency of ca. 93%. On close examination of the *cis*-stilbene spectrum, we believe this is reasonable. At 366 nm, near the leading edge of the 9CP absorption, there is a small absorbance from cSt ($\epsilon \approx 0.5\text{--}0.6 \text{ M}^{-1} \text{ cm}^{-1}$). Absorbance at 366 nm is required to account for our observation of direct valence isomerization at 366 nm, so we believe it to be real rather than due to impurities. It is commonly agreed that the absence of fluorescence from *cis*-stilbene arises from extremely rapid and efficient twisting about the $\alpha\beta$ bond in the excited state,^{2,17} which requires nonvertical, twisted excited singlet states at relatively lower energies. In such a case, a Franck-Condon envelope on S_1 absorption should decrease only relatively slowly with decreasing transition energy; cf. the much broader absorption for *cis*-stilbene compared to *trans* for their respective S_1 states. The more efficient sensitized access to the nonvertical excited states of *cis*-stilbene presumably results from the relatively long time scale available via bimolecular encounter or exciplex formation.

The rate constant we find for singlet excitation transfer to *cis*-stilbene is higher than values previously reported for collisional, endothermic singlet excitation transfer from arenes to either stilbene.¹⁸ We suggest that this rate enhancement results from the assistance of the polarity introduced by the cyano substituent. Whether or not an exciplex truly intervenes, this should enhance the interaction of the chromophores (if for no other reason than an electron transfer-Coulombic attraction mechanism which necessitates close approach of the chromophores to each other) and thus facilitate excitation transfer by an exchange mechanism. The importance of nonvertical excited states in enhancing triplet

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(18) Lewis, F. D.; Dalton, J. C.; Turro, N. J. *Mol. Photochem.* **1970**, 2, 67.

excitation transfer by an exchange mechanism was elegantly documented by Hammond et al. years ago.^{1,19} The rate of an exchange mechanism will not depend on the multiplicity of the states involved so long as spin is conserved,²⁰ and thus nonvertical singlet excitation is not a particular surprise. In view of the poor overlap of 9CP fluorescence and cSt absorption, Forster transfer and fluorescence-reabsorption mechanisms may obviously be ignored.

Thermal Stability of the Adducts. The ease of fragmentation on gas chromatography ranks the thermal stability of the adducts. Qualitatively, the unsubstituted phenanthrene-*trans*-stilbene adduct is the most resistant to thermal fragmentation, with the evidently quite strained 9CP-*cis*-stilbene adduct the most labile. *Trans* adducts from 9-cyanophenanthrene and the dicyanophenanthrene are intermediate. This ranking reflects a combination of expected biradical stability and ground-state strain relief. We cannot rule out a polar contribution to the thermolysis transition state.

Discussion

Comparison of Cycloaddition Reactivity with Theoretical Predictions. The results show that *trans*-stilbene, and its substituted analogues, are excellent cycloaddends for the phenanthrene chromophore. Reaction is observed to be efficient, and exciplexes are short-lived or absent in all the cases studied. We have previously pointed out¹⁴ that short-lived or undetectable exciplexes in cycloaddition systems normally may be taken as evidence for very rapid cycloaddition. We have recently presented an algorithm,⁵ based on current theory for allowed photocycloaddition,²¹ which permits an analysis of the factors which influence photocycloaddition reactivity and also permits prediction of reactivity for arbitrary allowed reactions. Factors presaging high reactivity are high singlet energy for the excited photoreactant, low triplet energy for both, and high frontier (HOMO and LUMO) orbital coefficients at reacting positions for both. Low E_T is advantageous because the singlet D state, the doubly excited configuration of reactants which correlates directly to the ground state of product, generally corresponds to overall singlet coupling of the two reactant lowest triplets and its energy is thus the sum of their triplet energies.

Our central purpose in the present study was to examine the reactivity of the phenanthrene-stilbene system for comparison against prediction. The γ value calculated for the unsubstituted phenanthrene-*trans*-stilbene reaction is 19.4 kcal/mol and for 9-cyanophenanthrene-*trans*-stilbene, 18.2 and is comparable for the other reactions of phenanthrenes and *trans*-stilbenes. This is in the highly reactive range,⁵ and consequently our observations in these cases are entirely consistent with theory.

The *Cis* Adduct 3bk. Qualitatively, the observation of 3bk in reaction of *cis*-stilbene with 9-cyanophenanthrene is remarkable in two respects. First, it represents the first photoaddition involving *cis*-stilbene. Second, the fact that both phenyls are endo is an even more striking example of the dominance of electronic (i.e., remote orbital interactions) over steric factors in cycloadditions involving exciplexes than those we presented previously. It appears necessary that the transition state for cycloaddition be an early one to account for the lack of importance of steric hindrance.

Quantitatively, *cis*-stilbene is less reactive than *trans*. The phenomenological second-order rate constant for cycloaddition of *cis* to 9-cyanophenanthrene is ca. $9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, while for *trans* it is $2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The relative reactivity is understandable from either electronic or steric considerations, but we feel that the former is the more important. Note that the known E_T for *cis*-stilbene (57 kcal/mol) aligns it more closely with the less reactive styrenes than with *trans*-stilbene (49 kcal/mol), as

does the second-order rate constant for cycloaddition. Since simple HMO coefficients presume a planar π system and since *cis*-stilbene cannot be planar, it is not possible to give a precise γ value for cycloadditions involving *cis*-stilbene. However, the value of γ (23.5 kcal/mol) calculated for reaction of a planar *cis*-stilbene with 9-cyanophenanthrene is in the range for moderate reactivity, and the value (21 kcal/mol) calculated for a planar styrene chromophore with a 90° twisted phenyl is not too different. We conclude that the reactivity of *cis*-stilbene and the phenanthrene chromophore can be understood from electronic factors alone and that steric hindrance is not necessary to account for the lowered reactivity relative to *trans*.

Effect of Charge Transfer. How Important Are Exciplexes?

Our present results show that the presence of substituents which support charge transfer is not a necessity in the highly reactive phenanthrene-stilbene system,⁶ in contrast to the phenanthrene-styrene system. A good yield of cycloadduct is isolated for the parent case 3aj. This reaction is, however, somewhat slower than the rest. Both cyano and methoxy groups enhance charge transfer and the quenching rates are higher. It is not easy to compare the parent case kinetically with the ones for which exciplex formation is obvious, because in the former one obtains a second-order rate constant quenching and in the latter one can (and must) dissect this bimolecular process into bimolecular exciplex formation and unimolecular exciplex decay. We have previously analyzed the role of exciplexes in cycloaddition as largely entropic^{14,22} and noted that, when they become very stable, exciplex collapse to adduct becomes less rapid.¹³

The rate of $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for quenching of phenanthrene singlet by *trans*-stilbene, though apparently low, is actually higher than we expect for a cycloaddition proceeding without exciplex formation. We have previously noted that the summation of entropy terms for exciplex formation and for exciplex collapse to cycloadduct in closely related systems is approximately -30 entropy units.²² Assuming that this same value would obtain for the case in which no exciplex intervened, i.e., that the overall entropy change in the latter is the sum of the changes for the two steps in the former, one calculates a maximum rate constant (for $\Delta H^\ddagger = 0$), for a reaction proceeding without prior formation of an exciplex, in the neighborhood of $10^6 \text{ M}^{-1} \text{ s}^{-1}$. The higher rate constant for *trans*-stilbene quenching of phenanthrene in fact suggests to us that an exciplex probably intervenes, making quenching more efficient, and that its relative lack of polarity allows it to avoid the potential well of the more polar, more stable exciplexes¹³ and collapse very rapidly to product. Judging from the fast quenching rate and the absence of exciplex emission for 9-cyanophenanthrene-*trans*-stilbene, that case also falls in this category.

Quantitative Comparison of *trans*-Stilbenes and Styrenes as Addends for Phenanthrenes.

Stilbenes are predicted to be better addends for phenanthrene than styrenes.⁵ The ratio of phenomenological second-order rate constants for quenching of 9-cyanophenanthrene singlet by *trans*-stilbene and β -methylstyrene is ca. 33. Neither experiment involves a fluorescent exciplex. From known redox parameters,^{23,24} the former exciplex would show an enthalpy of stabilization of only -1.6 kcal/mol. To determine the relative propensity for a stilbene vs. a styrene exciplex to collapse to product, we require a pair in which exciplex formation occurs with equal exothermicity. In such a case, a higher rate for exciplex collapse to product could be ascribed to a higher intrinsic reactivity and not to variation in exciplex stabilization. As it happens, *p*-methoxystilbene and 9-cyanophenanthrene form an exciplex ($\tau = 3.6 \text{ ns}$, ϕ cycloaddition ≈ 0.3) with a calculated enthalpy of formation of -12.2 kcal/mol (from $E_{ox} = +1.04 \text{ V}$ in CH_3CN vs. aqueous SCE), the latter value being within experimental error of the previously studied²³ 3,10-dicyanophenanthrene-*trans*-anethole exciplex (-12.7 kcal/mol). The former thus shows a rate of collapse to products of ca. 10^8 s^{-1} ;

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(20) For a discussion of excitation transfer by an electron-exchange mechanism, see: Turro, N. J. "Modern Molecular Photochemistry"; Benjamin-Cummings Publishing Co.: Menlo Park, CA, 1978; Chapter 9, pp 305-309 and 321-328.

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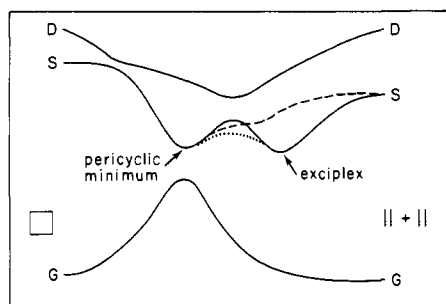


Figure 3. Schematic potential energy surfaces showing the relative barriers to cycloaddition for exciplexes of 9-cyanophenanthrene with *p*-methoxystilbene (···) and *trans*-stilbene (---) and of 3,9-dicyanophenanthrene with *trans*-anethole (—). See text.

cf. the latter¹³ at $4.6 \times 10^6 \text{ s}^{-1}$. The two situations are sterically very similar, and the ratio of rate constants (22) is similar to the styrene/stilbene ratio mentioned above. We consequently conclude that the *trans*-stilbene chromophore is intrinsically ca. 30 times the more reactive toward the phenanthrene chromophore in cycloaddition, irrespective of the intermediacy of exciplexes. The theoretical prediction thus finds quantitative reinforcement. The situation is summarized pictorially in Figure 3.

Direction of Charge Transfer. There are few studies of photocycloadditions in which a change of substituents has altered the direction of the donor-acceptor relationship of the partners, without a basic change in the chromophore. Both 9-cyanophenanthrene-dimethoxystilbene and phenanthrene-dicyanostilbene exciplexes form, and cycloaddition proceeds smoothly and rapidly in both cases. The former is a case in which the stilbene is clearly the donor, and in the latter one the phenanthrene must be the donor. The direction of charge transfer is thus not a determining factor. This is yet another manifestation that charge transfer is primarily advantageous in exciplex formation and stabilization but is considerably less relevant in exciplex collapse to products.

Trans Adduct Isomer Ratios. In only the unsymmetrical 9-cyanophenanthrenes are the 3 and 4 series of adducts distinct. In these cases the major product is always of type 3. Of the type 4 adducts, only 4bj and 4bp were actually isolated. By HPLC and NMR, the ratio of 3bj to 4bj is ca. 2.5:1, whether at low conversion or high, independent of the starting isomer. Inspection of the NMR of crude product mixtures from the other 9-cyanophenanthrenes shows that *trans*-stilbene generally produces a 2:1-3:1 ratio of type 3 to type 4 adduct. Unless remote orbital interactions are included, the ratio expected from an HMO perturbation calculation should be 1:1 since α and β coefficients of stilbene are identical by symmetry.

Quenching of Other Arene Singlets by the Stilbenes. Lewis, Dalton, and Turro have examined the rates of quenching of several aromatic hydrocarbon singlets by the stilbene isomers.¹⁸ The rate reported for quenching of phenanthrene singlet by *trans*-stilbene is twofold higher than we find. The geometric isomerization of *trans*-stilbene sensitized by chrysene singlet was reported. Singlet

excitation transfer was suggested to be the dominant quenching mechanism, as we believe is the case for 9-cyanophenanthrene singlet quenched by *cis*-stilbene. These authors did not examine the possibility of cycloaddition or valence isomerization.

Singlet-Sensitized Valence Isomerization. Energy Storage. To our knowledge there are no previous examples of singlet sensitization of strongly endothermic valence isomerization except the one mentioned below. Singlet sensitization of geometric isomerization of diphenylcyclopropanes,²⁵ and triplet sensitization of the norbornadiene-quadricyclane valence isomerization,²⁶ are known. "Exciplex isomerization", reported by Jones et al.²⁷ for some substituted Dewar benzenes, is a highly exothermic example of singlet-sensitized valence isomerization.

The norbornadiene-quadricyclane system, sensitized by visible absorbing sensitizers, has been proposed as a potentially useful scheme for the storage of solar energy.²⁸ The requirement for triplet sensitization, however, is one of the limiting factors. The energy difference $E_S - E_T = \Delta E_{ST}$ between lowest singlet and triplet states of the sensitizer is necessarily wasted, and this is always significant compared to E_S .

Jones has reported the singlet-sensitized valence isomerization of 2,3-bis(methoxycarbonyl)norbornadiene,²⁸ to our knowledge the only previous example of the mechanism with significant potential for energy storage. This and the present observation of singlet-sensitized endothermic valence isomerization of *cis*-stilbene suggest that the entire singlet energy of the sensitizer may in principle be used, a clear advance if it can be capitalized upon. However, the mechanism we suggest for the present case, singlet excitation transfer, is hardly a sure bet for improving significantly on direct excitation of the material undergoing valence isomerization. Excitation transfer from sensitizers absorbing strongly to the red of the reactant will be highly endothermic and thus quite inefficient. If, however, singlet sensitization can be used to access highly nonvertical and thus spectroscopically inaccessible excited states of reactant, the potential advantages of the process are much clearer. We are studying the idea in more detail and will report fully elsewhere.

Acknowledgment. We thank the Robert A. Welch Foundation for financial support through Grant AT-532. Flash kinetic measurements were made at the Center for Fast Kinetic Research at The University of Texas at Austin, funded by NIH Grant RR-0086 from the Biotechnology Branch of the Division of Research Resources and The University of Texas. Mr. John Gaudiello of The University of Texas at Austin performed the electrochemical measurements of *p*-methoxystilbene. We thank the Clark Foundation of Dallas for summer fellowships to P.E.H. and M.F.

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