

Picosecond Dynamics of *trans*-Stilbene Photodimerization[†]Kevin S. Peters,* Steven C. Freilich,[‡] and Joseph LeeDepartment of Chemistry and Biochemistry, University of Colorado,
Boulder, Colorado 80309-0215

Received: February 2, 1993; In Final Form: March 19, 1993

Picosecond absorption spectroscopy is used to examine the dynamics of the 2+2 photodimerization reaction of *trans*-stilbene in benzene. The quenching of the first excited singlet state of *trans*-stilbene by ground-state *trans*-stilbene occurs at the diffusion limit, $2.03 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Upon quenching, a new intermediate is formed with a λ_{max} of 480 nm which is characteristic of the charge-transfer species. The rate of the decay of the transient species is $(2.40 \pm 0.37) \times 10^9 \text{ s}^{-1}$. The assignment of the transient to the excimer or a biradicaloid species at the pericyclic minimum is discussed.

Introduction

The photochemistry of *trans*-stilbene continues to be extensively investigated.¹ Numerous kinetic studies of the *trans*-*cis* intramolecular isomerization reaction have critically examined theoretical formulations for both the nature of energy flow within reacting molecules²⁻⁴ as well as the influence of solvent dynamics on the reaction barriers.⁵⁻¹⁰ Surprisingly, there have been only a very limited number of mechanistic studies of the 2+2 photodimerization reaction of *trans*-stilbene.^{11,12} The mechanism of the reaction, as proposed by Lewis,¹³ involves the quenching of the first excited singlet state of *trans*-stilbene by ground-state *trans*-stilbene to form a nonfluorescent singlet excimer which subsequently collapses to cycloadduct. However, many questions remain concerning the mechanism for the photodimerization reaction. For example, although the kinetics for the formation of the excimer in benzene have been determined,¹⁴ the dynamics for the decay of the nonfluorescent singlet excimer have yet to be delineated. The solvent dependence of these processes is undefined. Also, the nature of the biradicaloid species at the pericyclic minimum on the excited potential energy surface has not been fully elucidated.

In this report we present a picosecond kinetic study of the 2+2 photodimerization of *trans*-stilbene in benzene. The kinetics for the quenching of the first excited singlet state of *trans*-stilbene to form a transient, which previously has not been observed, are examined. The absorption spectrum of the new transient species is obtained, and the kinetics for its decay are measured. Finally, the assignment of the transient species to either an excimer or a biradicaloid is discussed.

Experimental Section

Picosecond Absorption Spectrometer. The details of the picosecond absorption spectrometer have been presented previously.¹⁵ The spectrometer is based upon a Continuum (PY61C-10) Nd:YAG laser which yields light pulses with a fwhm of 19 ps at 10 Hz. Both third, 355 nm, and fourth, 266 nm, harmonics are used for excitation of the sample. The probe light, 400-800 nm, is produced by focusing the 1060-nm fundamental into a 10-cm cell containing a 1:1 mixture of H₂O-D₂O.

Single-wavelength kinetics are obtained by monitoring the *I* and *I*₀ beams, resolved by 5-nm narrow band pass filters, with photodiodes (EG&G DT100) coupled to two box car integrators (SRS 250) which are interfaced to a laboratory computer.

[†] Taken in part from the Ph.D. thesis of Steven C. Freilich, Harvard University, 1983.

[‡] Current address: Experimental Station, Central Research and Development Department, E. I. du Pont de Nemours and Co., Wilmington, DE 19898.

Transient absorption spectra are recorded by passing the *I* and *I*₀ beams into a JY 200 spectrometer interfaced to a Princeton Instruments thermoelectrically cooled CCD (TE/CCD 576 EUV).

Samples. *trans*-Stilbene (Aldrich) was recrystallized twice from absolute ethanol. Fumaronitrile (Aldrich) was dissolved in dichloromethane, the solution filtered, and the solvent rotary evaporated and then sublimed. Benzene (Mallinckrodt) was distilled over phosphorous pentoxide. Acetonitrile (Mallinckrodt) was distilled over CaH prior to use.

Data Analysis. The time-dependent absorbance *A*(*t*) obtained from the kinetic experiments results from the convolution of the instrument response function *I*(*t*) with the molecular kinetics *F*(*t*)

$$A(t) = \int_{-\infty}^t I(\tau) F(t-\tau) d\tau \quad (1)$$

where the instrument response function, *I*(*t*), is produced by the convolution of the pump and probe light pulse, each with a pulse width of σ , and is assumed to have the analytical form of a Gaussian,

$$I(t) = (2\pi\sigma)^{-0.5} \exp(-(t-t_0)^2/2\sigma^2) \quad (2)$$

The parameter *t*₀ is the position of the peak of the Gaussian. The value *t*₀ is defined as 0 ps following excitation of the sample. Monitoring the rise time of the S_n ← S₁ absorption for pyrene following 355-nm excitation, the width of the laser pulse, σ , is 19 ps and the fwhm of the instrument response function is 45 ps.

The analysis of the kinetic data assumes sequential first-order decays where the parameters for the kinetic model of *F*(*t*), eq 1, includes the absorbance of the transient species at the probing wavelength, *A_n*(λ), as well as an associated rate constant, *k_n*. The procedure for obtaining *A_n*(λ) and *k_n* from the kinetic data is to assume a kinetic model for *F*(*t*) and an initial set of values for *A_n*(λ) and *k_n* and then calculate *F*(*t*) which is convoluted with *I*(*t*) to give a calculated time-dependent absorbance, *A_{cal}*(*t*). The calculated *A_{cal}*(*t*) is then compared to the experimental time-dependent absorbance *A_{exp}*(*t*) through the sum of the square of the residuals, SSR.

$$\text{SSR} = \sum_i (A_{\text{exp}}(t) - A_{\text{cal}}(t))^2 \quad (3)$$

The value of SSR is then minimized through a nonlinear least-squares analysis to yield the optimum values for *A_n*(λ) and *k_n*.

Results

The transient absorption spectrum following the 355-nm irradiation of 0.4 M *trans*-stilbene (TS) in benzene is shown in

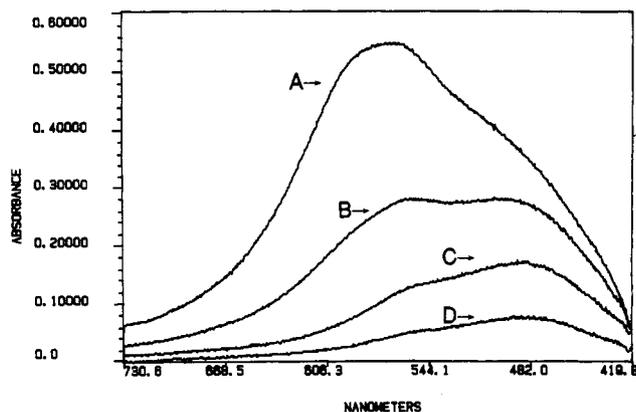


Figure 1. Transient absorption spectra following the 355-nm irradiation of 0.4 M *trans*-stilbene in benzene at 22 °C. Curve A, 0 ps; curve B, 100 ps; curve C, 300 ps; curve D, 700 ps.

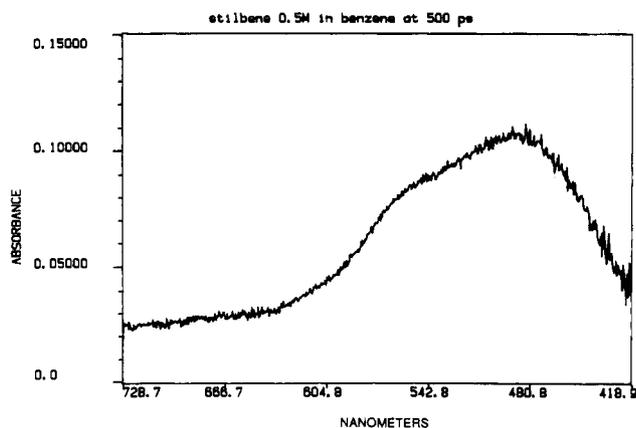


Figure 2. Transient absorption spectrum following the 355-nm irradiation of 0.4 M *trans*-stilbene in benzene at 22 °C at 500 ps.

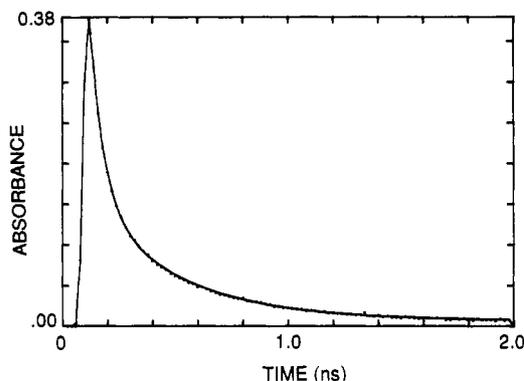


Figure 3. 540-nm dynamics following the 355-nm irradiation of 0.4 M *trans*-stilbene in benzene at 22 °C. Points: experimental data which are the average of five experiments, 20-ps time increments. Solid curve: calculated kinetics, $k_1 = 1.58 \times 10^{10} \text{ s}^{-1}$, $k_2 = 2.53 \times 10^9 \text{ s}^{-1}$, $A_1 = 0.528$, $A_2 = 0.142$, $\sigma = 19 \text{ ps}$, $t_0 = 93 \text{ ps}$, $\text{SSR} = 8.34 \times 10^{-5} \text{ OD}^2$.

Figure 1. At 0 ps, a new absorption appears with a λ_{max} at 567 nm. The absorption spectrum decays on the 100-ps time scale. Similarly, there is a decay in absorption spectrum at 480 nm; however, the rate of decay occurs on a longer time scale. By 500 ps, a new absorption spectrum appears where the λ_{max} is 480 nm with a shoulder at 550 nm, Figure 2.

The time dependence of the transient absorption spectrum displayed in Figure 1 was monitored at 580 nm, Figure 3, and 480 nm, Figure 4. Each of the data sets represents the average of five separate experiments where each experiment averages 50 laser shots. The kinetics span a time domain of 0–2 ns, with time increments of 20 ps. The estimated error in the optical absorbance for each data point is 0.001 OD.

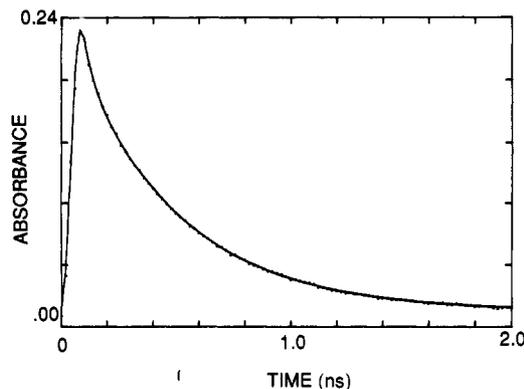


Figure 4. 480-nm dynamics following the 355-nm irradiation of 0.4 M *trans*-stilbene in benzene at 22 °C. Points: experimental data which are the average of five experiments, 20-ps time increments. Solid curve: calculated kinetics, $k_1 = 1.56 \times 10^{10} \text{ s}^{-1}$, $k_2 = 2.35 \times 10^9 \text{ s}^{-1}$, $A_1 = 0.328$, $A_2 = 0.205$, $\sigma = 19 \text{ ps}$, $t_0 = 90 \text{ ps}$, $\text{SSR} = 1.32 \times 10^{-4} \text{ OD}^2$.

TABLE I: Kinetic Parameters for the Decay of the Transient Species Monitored at 580 and 480 nm following the 355-nm Irradiation of *trans*-Stilbene in Benzene

concn of TS, M	$k_1 (\times 10^{10} \text{ s}^{-1})$	$k_2 (\times 10^9 \text{ s}^{-1})$
	580 nm	
0.2	1.12	2.30
0.3	1.26	2.25
0.4	1.58	2.53
0.5	1.69	2.56
	480 nm	
0.4	1.56	2.35
0.5	1.71	2.46

The simplest kinetic model that adequately characterizes the decay kinetics shown in Figures 3 and 4 is one where there are two sequential decays; a model incorporating two simultaneous decays was found not to reproduce the experimental data.



Four parameters are varied during the fitting procedure: the absorbance of transient species A_1 and A_2 , and the two associated rate constants, k_1 and k_2 . Species A_3 was assumed not to absorb at 580 and 480 nm. The kinetic parameters for the best fits of the model given in eq 4 to the experimental data displayed in Figures 3 and 4 are given in Table I. The values for the SSR, eq 3, for the kinetic data at 580 and 480 nm are $8.34 \times 10^{-5} \text{ OD}^2$ and $1.32 \times 10^{-4} \text{ OD}^2$, respectively. These values correspond to an average error in the fit of the kinetic model to the experimental data of 0.0009 OD at 580 nm and 0.0011 OD at 480 nm. These values are within the estimated error of the experimental data.

The kinetics for the decays at 580 and 480 nm were then measured as a function of the concentration of TS which was varied from 0.2 to 0.5 M (Table I). With increasing concentration, the rate associated with the first decay, $A_1 \rightarrow A_2$, increases from 1.12×10^{10} to $1.69 \times 10^{10} \text{ s}^{-1}$. Assuming the concentration dependence of the observed rate constant, k_1 , can be expressed as

$$k_1 = k_0 + k_q[\text{TS}] \quad (5)$$

then $k_0 = (7.02 \pm 0.42) \times 10^9 \text{ sec}^{-1}$ and $k_q = (2.03 \pm 0.08) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The rate constant for the second decay, $A_2 \rightarrow A_3$, is independent of the concentration of TS with an average value of $(2.40 \pm 0.37) \times 10^9 \text{ s}^{-1}$.

To aid in the characterization of the transient absorption spectra displayed in Figure 1, the absorption spectrum of the first excited singlet state of TS (TS^*) was measured following the 266-nm irradiation of 0.6 mM TS in acetonitrile. The species shown in Figure 5, having a λ_{max} at 575 nm, appears within the laser pulse and decays with a rate constant of $(1.92 \pm 0.29) \times 10^{10} \text{ s}^{-1}$.¹⁵

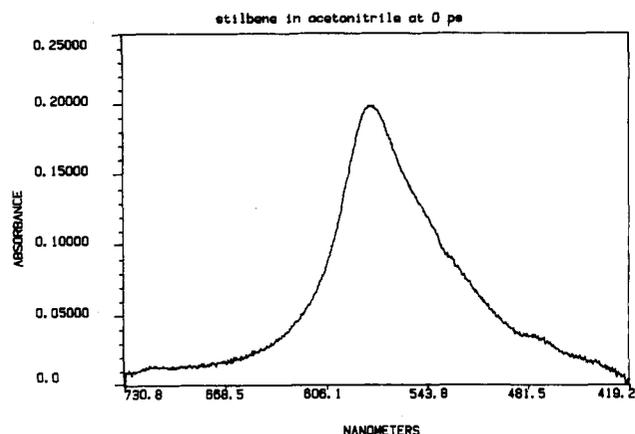


Figure 5. Transient absorption spectrum following the 266-nm irradiation of 0.6 mM *trans*-stilbene in acetonitrile at 22 °C at 0 ps.

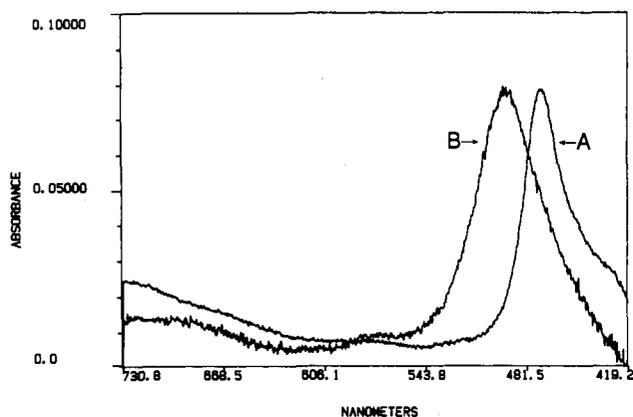


Figure 6. Curve A: transient absorption spectrum following the 355-nm irradiation of 0.125 M fumaronitrile, 0.025 M *trans*-stilbene in acetonitrile at 25 ps. Curve B: transient absorption spectrum following the 266-nm irradiation of 0.5 M dioxene, 0.6 mM *trans*-stilbene in acetonitrile at 100 ps.

The absorption spectrum of the radical cation of TS (TS^+) and the radical anion of TS (TS^-) may be obtained following the irradiation of TS in the presence of electron-poor or electron-rich olefins. In previous experiments we have shown that the 355-nm irradiation of the ground-state charge-transfer complex between TS and fumaronitrile results in the direct transfer of an electron from TS to fumaronitrile producing TS^+ and the radical anion of fumaronitrile.¹⁵ The absorption spectrum of TS^+ with λ_{max} 472 nm is shown in Figure 6. The TS^- may be formed by the irradiation of TS in the presence of dioxene, an electron-rich olefin, which quenches the TS^* to form TS^- and the radical cation of dioxene. The absorption spectrum of TS^- with λ_{max} 494 nm is displayed in Figure 6.

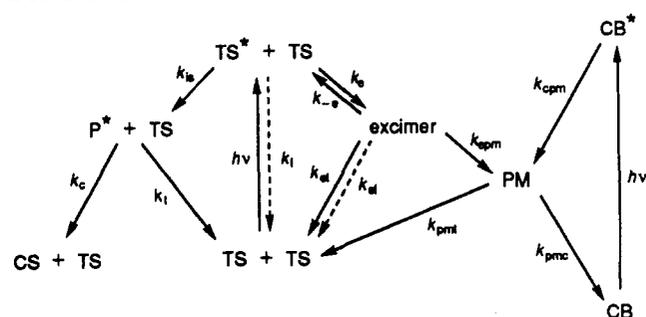
Discussion

Based on numerous experimental and theoretical studies of 2+2 photocycloaddition and photodimerization reactions, the mechanism for TS photodimerization is presented in Scheme I.¹⁶⁻²¹

In the absence of bimolecular quenching, TS^* decays by either fluorescence, k_f , or isomerization on the S_1 energy surface to the twisted P^* state, k_{is} , which then undergoes internal conversion to the ground-state surface partitioning between TS, k_i , and *cis*-stilbene (CS), k_c .¹ The intersystem crossing of TS^* at room temperature is negligible. The radiative lifetime of TS^* is approximately 2 ns. The quantum yield for *trans* \rightarrow *cis* photoisomerization is 0.50 in the absence of bimolecular quenching of TS^* .

In the presence of ground-state TS, it has been proposed¹³ that TS^* is quenched by TS to form an excimer, k_e ; the excimer is

SCHEME I



believed to be formed irreversibly.¹⁴ In turn, the excimer may decay back to ground-state TS by fluorescence, k_{ef} , or by back electron transfer, k_{et} . In addition, the singlet excimer may undergo intersystem crossing to form the triplet excimer which in turn decays by back electron transfer to form triplet *trans*-stilbene, processes not depicted in Scheme I. A final decay pathway for the excimer is collapse to a biradicaloid species at the pericyclic minimum (PM), k_{cpm} , which upon internal conversion partitions between the cyclobutane adduct (CB), k_{pmc} , and ground-state TS, k_{pmt} . In benzene, the limiting quantum for CB formation from the PM is 0.8 ± 0.2 .¹² The PM can also be accessed from the photocycloreversion of CB through irradiation of CB to form the excited single state of CB (CB^*) which then decays to PM, k_{cpm} . The nature of the electronic structures as well as the reaction dynamics for the excimer and the biradicaloid are unknown.²²

In view of the above mechanism, the first intermediate that is observed following irradiation of TS is TS^* . Upon 355-nm irradiation of 0.4 M TS in benzene, there appears a new species at 0 ps with an absorption maximum at 567 nm which is assigned to the TS^* absorption ($S_n \leftarrow S_1$) (Figure 1). When the absorption spectrum of TS^* is recorded in acetonitrile following the 266-nm irradiation of 0.6 mM TS, a similar spectrum appears at 0 ps with a λ_{max} 575 nm (Figure 5). However, there is a clear solvent effect upon the absorption spectrum of TS^* for the absorption band is narrower in acetonitrile as compared to benzene. Also, we have found that the profile for the absorption spectrum of TS^* in cyclohexane is virtually identical to that in acetonitrile.²³ A possible explanation for the diffuseness of TS^* absorption in benzene is a π -complex interaction between TS^* and TS given the high concentrations (0.4 M) TS. This would necessitate an initial ground-state π -complex interaction between TS^* 's. Evidence for such an interaction has been found for phenanthrene-9-carbonitrile in dichloromethane.²⁴ However, this rationale is unlikely as it was shown that the kinetics for the quenching of TS^* depends linearly upon TS concentration, eq 5, over the range of 0.2–0.5 M and is diffusion limited, $2.03 \times 10^{10} M^{-1} s^{-1}$, ruling out a ground-state molecular association between TS^* 's. A more likely explanation is that there is a π -complex between TS^* and benzene which modifies the potential energy surface for TS^* leading to a broader absorption band. Unfortunately, it was not possible to obtain the TS^* absorption band at low concentrations of TS in benzene by irradiation at 266 nm, for at this wavelength there is a strong absorption by the solvent benzene.

The intrinsic rate for the decay of TS^* in the absence of bimolecular quenching was determined by extrapolation of the observed rate k_1 , eq 5, to zero concentration of TS. The value is $7.02 \times 10^{10} s^{-1}$, corresponding to a lifetime of 143 ps, reflecting the sum of the processes k_{is} and k_f . Since the value of k_f is approximately $5 \times 10^8 s^{-1}$, the rate for the isomerization of TS^* along the excited-state surface, k_{is} , is $6.5 \times 10^9 s^{-1}$. The bimolecular quenching of TS^* by TS is $2.03 \times 10^{10} M^{-1} s^{-1}$ corresponding to the diffusion limit in benzene.

The spectrum of the transient species resulting from the bimolecular quenching of TS^* by TS is shown in Figure 2. This species decays with rate $2.34 \times 10^9 s^{-1}$, a process which is

independent of the concentration of TS. This kinetic behavior is consistent with that associated with the excimer. The excimer can be viewed as being derived from a resonance hybrid of a locally excited singlet state, TS^* , and a charge-transfer state composed of the radical cation of TS (TS^+) and the radical anion of TS (TS^-).²²

$$\Psi_{\text{excimer}} = a\Psi(TS^*) + b\Psi(TS^+TS^-) \quad (6)$$

If $\Psi(TS^*)$ were to make only a negligible contribution to Ψ_{excimer} , so that $b \gg a$, then the absorption spectrum of the excimer should appear as the sum of the absorption spectrum of TS^+ and TS^- . If the absorption spectrum in Figure 2 is that of the excimer, it does not correspond to the sum of the radical cation and radical anion of TS (Figure 6) as there is a significant absorbance at 550 nm which is not present in the absorption spectra for either the radical cation or radical anion of TS. Therefore, if the transient species is an excimer, then Ψ_{excimer} must contain a significant contribution of $\Psi(TS^*)$.

If it is argued that both $\Psi(TS^*)$ and $\Psi(TS^+TS^-)$ make significant contributions to Ψ_{excimer} , then TS^* and radical ion pair TS^+TS^- must be close in energy.²² Indeed there are many instances where the excimer is known to decay through an excited singlet state.¹⁸ In the analysis of the kinetic data shown in Figures 3 and 4, it was assumed that TS^* decayed in a unimolecular fashion to give rise to the excimer, k_e . To see if there is kinetic evidence for the reversion of the excimer to TS^* , k_{-e} , in the experimental data, we expanded the kinetic model to include this process and found that k_{-e} evolved to a significantly small value and furthermore there was no improvement in SSR, eq 3. Thus, we found no evidence in the experimental data for excimer reversion to TS^* , supporting the conclusions of Lewis that the excimer is formed irreversibly.¹⁴

An alternative assignment for the transient species displayed in Figure 2 is a biradicaloid species located at the pericyclic minimum. This would necessitate that the kinetics for the collapse of the excimer to the biradicaloid, k_{epm} , is greater than k_e , the quenching of TS^* by TS. In a previous picosecond study²¹ of a covalently linked anthracenes, bis(9-anthryl)methanol, and its corresponding 4+4 cycloadduct, irradiation of either species produced a common intermediate which was assigned as a biradicaloid located at the pericyclic minimum; the rate of its decay is $7.6 \times 10^8 \text{ s}^{-1}$. This rate is similar to the rate of decay for the species depicted in Figure 2. In addition, the absorption

spectrum of the biradicaloid species was very similar to the superposition of the radical anion and radical cation absorption spectrum of anthracene.²¹

Thus, based upon kinetic and spectral properties, it is not possible to unequivocally assign the transient species shown in Figure 2 to either the excimer or a biradicaloid at the pericyclic minimum. In the future, we hope to undertake a picosecond study of the photocycloreversion of tetraphenylcyclobutane to see if a transient species identical to that in Figure 2 intervenes in the photocleavage to form TS. A previous 15-ns flash photolysis study of tetraphenylcyclobutane failed to find such a transient species.²⁵ If such a species is produced upon photocycloreversion, this would lend strong support to the assignment of the transient species to the biradicaloid.

Acknowledgment. This work is supported by a grant from the National Science Foundation, CHE 9120355.

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