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# *cis*-Stilbene Photochemistry: Solvent Dependence of the Initial Dynamics and Quantum Yields

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**Abstract:** Photochemical quantum yields for the formation of *trans*-stilbene and 4a,4b-dihydrophenanthrene from *cis*-stilbene have been measured in cyclohexane, hexane, acetonitrile, and methanol solvents. Degassed *cis*-stilbene samples at 27 °C were irradiated at 280 nm, and the formation of photoproducts was monitored by absorption spectroscopy. The quantum yield for formation of dihydrophenanthrene is two to three times greater in the nonpolar solvents than in the polar ones (15–19% vs 5–8%), while a slight solvent dependence of the yield of *trans*-stilbene is observed (35–39% in the polar solvents vs 32–35% in the hydrocarbons). Ground-state resonance Raman spectra of *cis*-stilbene have also been obtained with 266-nm excitation in each of the four solvents in order to probe the initial dynamics of nuclear motion in the Franck–Condon region. The intensities suggest very slightly faster distortion of the vertically excited state along out-of-plane and hydrogen wagging and rocking coordinates in polar relative to nonpolar solvents. The implications for the dynamics of the *cis–trans* isomerization and ring closure reactions are discussed.

## Introduction

The photoreactions of *cis*- and *trans*-stilbene have been studied extensively as models for large-amplitude barrierless and barrier crossing reactions in both vapor and solution phases (for an excellent recent review, see ref 1). *trans*-Stilbene undergoes only one important primary photoreaction, the *trans-cis* isomerization, and this reaction has been studied in great detail through traditional photochemical methods,[2-4] time-resolved laser techniques,[5-22] and theory.[13,22-25] *cis*-Stilbene, in contrast, undergoes not only *cis–trans* photoisomerization but also a photochemical ring closure reaction to form 4a,4b-dihydrophenanthrene (DHP) (Figure 1). Early photochemical studies established the identity of the two major products and the excited singlet state pathway for both photoreactions.[26-29] However, due to the very short lifetime of *cis*–stilbene's excited state, studies of the dynamics were few and far between until recently and generally focused on the major *cis–trans* isomerization pathway.[30-33] During the past few years the ultrafast photochemistry of *cis*-stilbene has been probed by a variety of techniques including transient absorption,[34-40] time-resolved fluorescence,[41,42] steady-state flu-

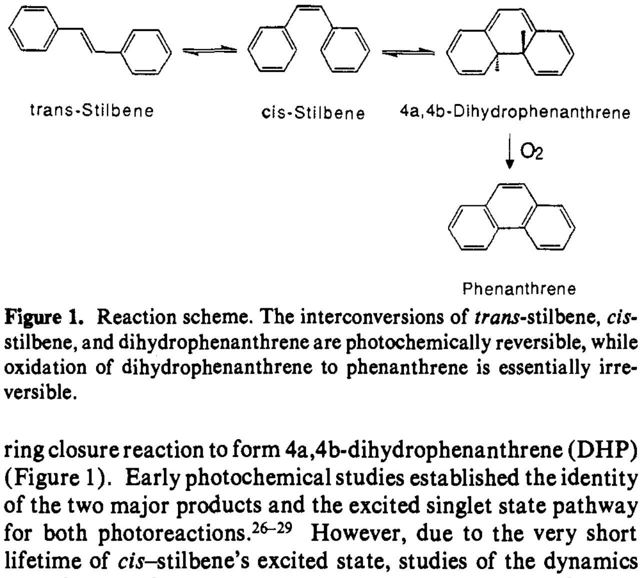

**Figure 1.** Reaction scheme. The interconversions of *trans*-stilbene, *cis*-stilbene, and dihydrophenanthrene are photochemically reversible, while oxidation of dihydrophenanthrene to phenanthrene is essentially irreversible.

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orescence,[43,44] transient resonance Raman,[45,46] and spectroscopy of isolated molecules and clusters cooled in supersonic jet expansions.[47-49] The photocyclization reaction to form DHP has been a partial or major focus of several of these studies.

Recent experimental results from several groups point to significant solvent effects on the photochemistry of *cis*-stilbene. The excited-state lifetime of *cis*-stilbene, measured by either transient absorption or time-resolved fluorescence techniques, has been found to be generally shorter in polar than in nonpolar solvents.[37,39,40,42] This suggests that the excited state distorts more rapidly along either the double-bond torsion or ring-closure coordinates, or both, in polar solvents, and is qualitatively consistent with the observation of generally faster isomerization of *trans*-stilbene in polar versus nonpolar solvents having comparable viscosities. Our group, in the course of obtaining the resonance Raman spectrum of DHP, observed that the ratio of photochemically generated DHP to *trans*-stilbene appeared to be greater in cyclohexane than in methanol.[45] That result indicated a solvent effect on the *cis*-stilbene → *trans*-stilbene and/or *cis*-stilbene → DHP quantum yields.

In view of the very short excited state lifetime of *cis*-stilbene, it is reasonable to surmise that the overall photochemical product yields and/or branching ratios may be strongly influenced by the initial dynamics of nuclear motion near the vertically excited geometry. These dynamics may be deduced from the Raman intensities of the *cis*-stilbene ground state excited on resonance with the photoreactive electronic state.[32,50-52] In this study, we examine the solvent dependence of *cis*-stilbene's photoreactions through two different, complementary experimental techniques. First, the quantum yields for the *cis* → *trans* and *cis* → DHP reactions are determined in two polar and two nonpolar solvents by irradiation of ground-state *cis*-stilbene with a narrow bandwidth cw lamp followed by quantitation of the photoproduct concentrations by absorption spectroscopy. Second, the resonance Raman intensities of *cis*-stilbene are measured in the same four solvents to determine the initial dynamics of motion in the Franck–Condon region. In this way we aim to explore the connection between the initial nuclear dynamics and the net photochemistry for these ultrafast reactions.

## Experimental Section

*Cis*-Stilbene (Aldrich) and hexane, cyclohexane, acetonitrile, and methanol, all HPLC or spectroscopic grade, were used as received. For the photochemical yield experiments, 3 mL samples of *cis*-stilbene in each solvent were degassed to $10^{-6}$ Torr by repeated freeze–pump–thaw cycles on a vacuum line and were then sealed in their 1-cm path length fused silica cuvettes. The samples were irradiated with a Photon Technology International Quantacount consisting of a Hg-Xe lamp transmitted through a monochromator to provide excitation centered at 280 nm with a bandpass of 4 nm. The total number of photons absorbed was monitored with an actinometer using actinochrome 1R. Samples were thermostatted at 27 °C throughout the experiments. UV–visible absorption spectra were recorded periodically with Hewlett-Packard 8451A diode array or IBM scanning spectrophotometers to monitor the photoreactions. Four separate experiments were performed to determine the photoproduct yields.

(1) The yields for DHP production were determined by irradiating concentrated (10 mM) *cis*-stilbene samples, which allowed readily detectable concentrations of the blue-absorbing DHP to build up without converting a significant fraction of the starting material. Absorption spectra in the 350–550-nm region were recorded after every $4.7 \times 10^{-8}$ Einsteins absorbed, and the DHP concentrations were calculated from the absorbances at the $\lambda_{max}$ (445–450 nm) assuming a solvent-independent molar extinction coefficient of 6750 $M^{-1}\,cm^{-1}$.[28] The DHP quantum yields were calculated from the absorbances after a total light dose of $8.9 \times 10^{-7}$ Einsteins, at which point only about 3% of the *cis*-stilbene molecules had absorbed a photon.

(2) The yields for *trans*-stilbene production had to be determined under conditions of higher photoconversion, since both stilbene isomers absorb only in the UV. Spectra of 0.055 mM samples were recorded every $4.7 \times 10^{-8}$ Einsteins absorbed, corresponding to absorption of a photon by ≈28% of the *cis*-stilbene molecules. The UV absorption spectrum in the 250–330-nm range, consisting of a mixture of contributions from both stilbene isomers and DHP, was then fit to a weighted sum of the spectra of all three species using a multiple linear regression method with the concentration of DHP constrained to the value determined from the visible absorbance. The method of analysis is described in more detail in ref 53. The UV absorption spectrum of DHP was estimated from Figure 4 of ref 28. The quantum yields for *trans*-stilbene formation were then determined from the initial slopes of the plots of the *trans*-stilbene concentration vs absorbed quanta.

(3) The *trans*-stilbene and DHP yields were determined in separate experiments by irradiating low concentration samples as in experiment (2) until $4.4 \times 10^{-8}$ Einsteins had been absorbed and then exposing the samples to air to oxidize the DHP to phenanthrene. The concentrations were then determined by fitting the resulting UV absorption spectra as described in (2) above to a sum of the spectra of both stilbene isomers and phenanthrene. Three to eight runs on separately prepared solutions were performed in each solvent. Although phenanthrene was present in rather low concentrations, it has a more structured absorption spectrum and a higher extinction coefficient than either stilbene isomer, making it possible to obtain quite accurate concentrations in this manner. The advantage of this approach is that the stilbenes and phenanthrene are all stable species whose UV spectra and extinction coefficients are known accurately.

(4) The rate of thermal decay of DHP at 27 °C was determined by generating an initial concentration of DHP as in method (1) above, leaving the sample in the dark, and recording the visible absorption spectrum at 1-min. intervals.

Resonance Raman spectra of ground state CS were obtained in all four solvents with 266 nm excitation (≈100 μJ/pulse) using the apparatus and methods described in detail previously.[54,55] Sample concentrations were approximately 4.6 mM. The spectra were calibrated in wavenumber using the Raman bands of cyclohexane and were corrected for reabsorption and detection sensitivity and the integrated peak areas determined as described elsewhere.[54,55]

## Results

The thermal decay of DHP at 27 °C over a period of 60 min was adequately fit as a first-order decay with an essentially solvent-independent (within ±10%) rate constant of $7.5 \times 10^{-5}\ s^{-1}$. The decrease in the concentration of DHP over the longest irradiation time involved in our photochemical experiments (20 min) is only about 9%. The thermal decay of DHP was neglected in our subsequent analyses of the photochemical conversion rates.

Figure 2 plots the DHP concentration, determined from the visible absorbance as described in method (1) above, as a function of the number of absorbed photons for *cis*-stilbene samples of equal initial concentration in all four solvents. It is clear that the

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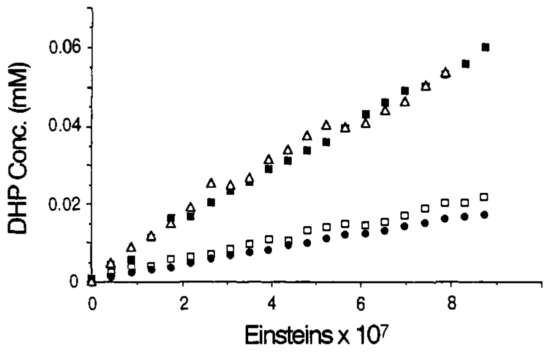

**Figure 2.** Plot of dihydrophenanthrene concentration as a function of moles of photons (Einsteins) absorbed by *cis*-stilbene samples in hexane (closed squares), cyclohexane (open triangles), methanol (open squares), and acetonitrile (closed circles). Initial *cis*-stilbene concentrations were 10 mM in a 3-mL volume.

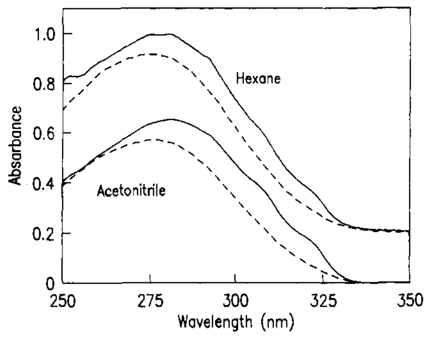

**Figure 3.** Absorption spectra of *cis*-stilbene samples in hexane (top, vertically offset) and in acetonitrile (bottom) before irradiation (dashed) and after absorption of 4.4 × $10^{-8}$ Einsteins followed by air oxidation of DHP to phenanthrene (solid). Initial *cis*-stilbene concentrations were 0.055 mM in a 3-mL volume.

**Table I.** Photochemical Quantum Yields for *cis*-Stilbene[a]

| | $\phi_{\text{cis}\rightarrow\text{trans}}$ | | $\phi_{\text{cis}\rightarrow\text{DHP}}$ | |
|---|---|---|---|---|
| solvent | method 2[b] | method 3[c] | method 1[d] | method 3[c] |
| methanol | 37 ± 5 | 38.2 ± 0.7 | 7 ± 1 | 7.7 ± 2.7 |
| acetonitrile | 35 ± 5 | 38.6 ± 0.8 | 6 ± 2 | 4.8 ± 0.8 |
| hexane | 33 ± 3 | 32.3 ± 0.9 | 19 ± 2 | 15.5 ± 1.6 |
| cyclohexane | 35 ± 3 | 34.5 ± 2.2 | 18 ± 2 | 17.4 ± 0.3 |

[a] Quantum yields multiplied by 100. Temperature 27 °C, irradiation wavelength 280 nm for all experiments. [b] By fitting of the UV spectra of oxygen-free samples to a sum of *cis*-stilbene, *trans*-stilbene, and DHP spectra. [c] By air oxidation of irradiated samples followed by fitting of the UV spectra to a sum of *cis*-stilbene, *trans*-stilbene, and phenanthrene spectra. [d] By direct measurement of DHP visible absorbance.

quantum yield for forming DHP is much higher in the two nonpolar solvents (hexane and cyclohexane) than in the two polar ones (methanol and acetonitrile).

Figure 3 shows examples of spectra obtained from experiment (3) in both acetonitrile and hexane solvents. Clearly much more DHP is formed and oxidized to phenanthrene in hexane, as evidenced by the more pronounced peak at the phenanthrene absorption maximum of 252 nm. The spectrum in acetonitrile, on the other hand, exhibits stronger absorption features due to *trans*-stilbene near 308 and 320 nm.

Table I summarizes our photochemical quantum yields for the *cis*-stilbene → DHP and *cis*-stilbene → *trans*-stilbene reactions. The quantum yields for DHP formation determined by methods (1) and (3) above are in reasonably good agreement, with the yields being roughly a factor of three higher in the nonpolar solvents than in the polar ones. The systematically slightly higher values obtained from experiment (1) could reflect uncertainties in the literature value for the DHP absorption coefficient and may also be due in part to the fact that method (3) was not carried out under conditions of negligible conversion of the starting material; a single measurement from each sample was made after approximately 28% of the initially present *cis*-stilbene molecules had absorbed a photon. However, both experiments give comparable ratios of the DHP quantum yields in the different solvents. The literature value of $\phi_{\text{DHP}} = 0.1$, measured in methylcyclohexane/isohexane at 0 °C with 313-nm excitation,[28] falls between our polar and nonpolar solvent values. We find the yields for *trans*-stilbene formation to be slightly solvent dependent (higher in the polar solvents), bracketing the literature value of $\phi_{\text{TS}} = 0.35$ reported in both methylcyclohexane/isohexane and ethanol/methanol at 25 °C with 313-nm excitation.[56]

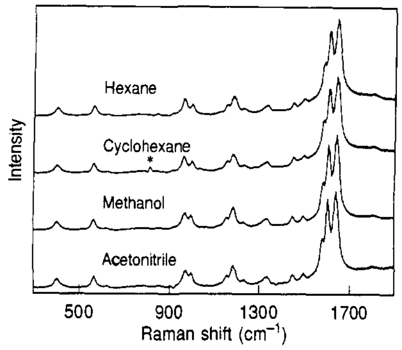

**Figure 4.** Resonance Raman spectra of 4.6 mM *cis*-stilbene in the indicated solvents with 266-nm excitation. Pure solvent spectra have been subtracted; an asterisk marks a solvent subtraction artifact in the cyclohexane spectrum.

**Table II.** Resonance Raman Intensities of *cis*-Stilbene[a]

| methanol | | acetonitrile | | hexane | | cyclohexane | |
|---|---|---|---|---|---|---|---|
| freq | rel int | freq | rel int | freq | rel int | freq | rel int |
| 405 | 10.0 | 405 | 11.2 | 403 | 9.4 | 403 | 10.5 |
| 563 | 9.6 | 563 | 10.1 | 561 | 8.7 | 561 | 8.6 |
| 969 | 20.4 | 971 | 19.4 | 964 | 16.3 | 963 | 14.6 |
| 999 | 6.6 | 999 | 8.0 | 1000 | 6.4 | 1000 | 6.7 |
| 1187 | 23.8 | 1187 | 24.8 | 1185 | 19.8 | 1185 | 17.8 |
| 1329 | 11.0 | 1330 | 9.6 | 1329 | 7.4 | 1326 | 9.1 |
| 1576 | 18.7 | 1575 | 19.4 | 1577 | 20.8 | 1577 | 20.7 |
| 1597 | 50.6 | 1594 | 49.5 | 1599 | 46.0 | 1599 | 47.0 |
| 1631 | 100 | 1630 | 100 | 1632 | 100 | 1632 | 100 |

[a] Frequencies in $\text{cm}^{-1}$; intensities in terms of integrated area relative to ethylenic C=C stretch.

Figure 4 presents the 266-nm excited resonance Raman spectra of ground-state *cis*-stilbene in all four solvents. The spectra are qualitatively very similar, but quantitative examination reveals some small but consistent differences. Table II summarizes the frequencies and relative integrated intensities of the nine strongest bands in the 400–1700-$\text{cm}^{-1}$ region of the *cis*-stilbene resonance Raman spectra. The largest solvent effect involves the 963–971-$\text{cm}^{-1}$ band, assigned as a predominantly hydrogen out-of-plane wagging vibration,[32,57] which shifts to higher frequency by 5–8 $\text{cm}^{-1}$ and increases its intensity (relative to the ethylenic C=C stretch) by 15–35% on going from the nonpolar to the polar solvents. As the positions and relative intensities of these reasonably strong Raman lines in a single solvent are typically reproducible to within about 2 $\text{cm}^{-1}$ and 10%, respectively, the observed variations among solvents exceed the experimental uncertainties. The bands at 561–563 $\text{cm}^{-1}$ (primarily C=C torsion), 1185–1187 $\text{cm}^{-1}$ (two overlapping lines, primarily C–$\phi$ stretch and in-plane CH rock), and 1326–1329 $\text{cm}^{-1}$ (mostly CH rock) also show both slightly higher frequencies and higher intensities in the polar solvents. The frequency changes indicate a solvent effect on the ground state conformation and/or electron distribution, while the increased intensities imply faster distortion

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**Table III.** Inferred Rate Constants for Decay Channels of Excited *cis*-Stilbene

| solvent | $\tau$ (ps) | $\phi_{cis\rightarrow trans}$ (this work) | $k_{twist}$ (ps$^{-1}$) [eq 3] | $k_{rc}$ (ps$^{-1}$) [eq 4] | $\phi_{cis\rightarrow DHP}$ (this work) | $F_{DHP}{*}k_{rc}$ (ps$^{-1}$) [eq 6] |
|---|---|---|---|---|---|---|
| hexane | 1.00 ± 0.02[a] | 0.33 ± 0.02 | 0.66 ± 0.04 | 0.34 ± 0.04 | 0.17 ± 0.02 | 0.17 ± 0.03 |
| cyclohexane | 1.65 ± 0.42[b] | 0.35 ± 0.03 | 0.46 ± 0.12 | 0.30 ± 0.06 | 0.18 ± 0.02 | 0.12 ± 0.04 |
| methanol | 0.50 ± 0.02[c] | 0.38 ± 0.02 | 1.52 ± 0.10 | 0.24 ± 0.04 | 0.07 ± 0.02 | 0.14 ± 0.05 |
| acetonitrile | 0.38[d] | 0.37 ± 0.03 | 1.95 ± 0.16 | 0.26 ± 0.06 | 0.05 ± 0.02 | 0.13 ± 0.05 |

[a] Range of lifetimes reported in refs 39 and 40. [b] Range of lifetimes reported in refs 37 and 42. [c] Range of lifetimes reported in refs 39, 40, and 42. [d] Lifetime from refs 39 and 42.

of the vertically excited state along both out-of-plane and in-plane hydrogen wagging coordinates in the polar solvents.

The solvent dependences of the absorption spectra of both *cis*-stilbene and DHP were also examined. The spectra of DHP have nearly the same bandshape in all four solvents and vary only slightly in position, with $\lambda_{max}$ ranging from 445 nm in methanol to 449 nm in cyclohexane. The spectra of *cis*-stilbene are even less solvent dependent, with $\lambda_{max}$ of the very broad band ranging only from ≈278 nm in hexane, methanol, and acetonitrile to ≈280 nm in cyclohexane.

## Discussion

It is well established that the excited-state lifetimes of the stilbene isomers exhibit a fairly significant dependence on solvent polarity. In *trans*-stilbene the lifetime depends most strongly on solvent viscosity but is also shorter in polar solvents than in nonpolar ones having comparable viscosities. Efforts to determine the activation energy for excited-state isomerization have generally resulted in much lower activation barriers in polar than in nonpolar solvents, although there is still some controversy over this matter. The situation is complicated by the likelihood that the lowering of the barrier in polar solvents is due largely to dynamic solvent polarization as the isomerization proceeds, such that the isomerization barrier is actually a time-dependent quantity.[1,15,18,19,58] Our very recent picosecond time-resolved anti-Stokes Raman experiments also show that the ground-state vibrational relaxation of *trans*-stilbene is significantly faster in methanol than in cyclohexane.[59] In any case, while the *dynamics* of *trans*-stilbene's excited-state isomerization are clearly sensitive to solvent polarity, there is no evidence that the quantum yields are. Double bond isomerization is the only important excited-state reaction *trans*-stilbene undergoes, and the partitioning from the presumed 90° twisted phantom state into the *cis* and *trans* ground states appears to be very nearly equal in different solvents.[10,56]

The excited-state lifetime of *cis*-stilbene has also been shown to be dependent on solvent polarity with polar solvents giving shorter lifetimes.[37,39,40,42] *cis*-Stilbene is, however, a more interesting case in that it has two important photoproducts. The present study shows clearly that nonpolar solvents give a much higher yield for ring closure and a slightly lower yield for isomerization as compared with the polar solvents. This, together with the slightly higher resonance Raman intensities for modes involving out-of-plane motion in the polar solvents, suggests that the principal effect of polar solvation is to speed up the motion along the twisting coordinate in the excited state, shortening the lifetime and also reducing the yield of the competing ring closure reaction.

This model can be quantitated as follows. We assume that the total rate of excited-state decay can be written as a sum of the rates of double bond twisting to form the phantom twisted state, $k_{twist}$, and of ring closure to form electronically excited DHP, $k_{rc}$ (radiative decay is neglected, as the natural radiative lifetime is roughly four orders of magnitude longer than the observed lifetimes):

$$k = 1/\tau = k_{twist} + k_{rc} \qquad (1)$$

We then assume that the phantom state partitions equally into the *cis* and *trans* ground states, so that the quantum yield for *trans*-stilbene formation is given by

$$\phi_{cis\rightarrow trans} = 0.5\phi_{twist} = 0.5(k_{twist}/k) = 0.5k_{twist}\tau \qquad (2)$$

The rate constant for twisting in the excited state of *cis*-stilbene therefore becomes

$$k_{twist} = 2\phi_{cis\rightarrow trans}/\tau \qquad (3)$$

while the corresponding rate constant for excited state ring closure is

$$k_{rc} = (1 - 2\phi_{cis\rightarrow trans})/\tau \qquad (4)$$

The fraction of electronically excited DHP molecules that partition to ground state DHP is left as an unknown, $F_{DHP}$ (Petek *et al.* take $F_{DHP}$ to be $^1/_3$ based on earlier quantum yield data, with the remaining $^2/_3$ returning to ground-state *cis*-stilbene[48]). The quantum yield for ground state DHP formation is then

$$\phi_{cis\rightarrow DHP} = F_{DHP}\phi_{rc} = F_{DHP}(k_{rc}/k) = F_{DHP}k_{rc}\tau \qquad (5)$$

and the product of the ring closure rate constant and the DHP partitioning fraction becomes

$$F_{DHP}k_{rc} = \phi_{cis\rightarrow DHP}/\tau \qquad (6)$$

Table III summarizes the measured excited-state lifetimes and *cis* → *trans* and *cis* → DHP quantum yields in the four solvents employed in this study, together with the rate constants for excited-state twisting and ring closure obtained from eqs 3, 4, and 6. The rate constant for twisting varies by more than a factor of 4 across this solvent series and is clearly much greater in the polar than in the nonpolar solvents, consistent with an increased slope of the excited state surface along the twisting coordinate in polar solvents. This could result from polar solvent stabilization of the highly polarizable and/or dipolar phantom state.[60,61] The inferred rate constant for ring closure also seems to vary considerably among solvents, but the uncertainties in this quantity are larger and the correlation with solvent polarity not as strong as for $k_{twist}$. In contrast, the product of the rate constant for ring closure and the fraction of excited DHP that partitions to ground state DHP varies by only about 35% among solvents, a variation that is not significant to within the combined uncertainties of the lifetime and quantum yield data.

There seems to be little doubt that *cis*-stilbene undergoes faster torsional isomerization in methanol and acetonitrile than in hydrocarbons of comparable viscosity (see also Table III), but the solvent dependence of the ring closure process remains somewhat controversial. Todd and Fleming measured *cis*-stilbene's fluorescence lifetime in a wide variety of solvents.[41,42] From these results, together with the lifetime data of other groups[30,34,37,39] and our group's preliminary quantum yields,[45] they concluded that the effect of solvent polarity on *cis*-stilbene's excited-state lifetime results mainly from an effect on the torsional isomerization coordinate rather than the ring closure. They proposed, however, that the shorter lifetime in polar compared with nonpolar solvents of the same viscosity arises not from changes

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in the potential energy surfaces but from changes in the proportionality between macroscopic viscosity and microscopic friction as a function of solvent size and type. Nikowa *et al.*, on the other hand, examined the pressure dependence of the lifetime and found that the nonradiative rate constant is well fit to the sum of a viscosity-independent term and one inversely proportional to viscosity, which they identified with the ring closure and torsional isomerization channels, respectively.[39] From the solvent dependence of these quantities, they concluded that the rate constants for both twisting and ring closure, and probably also the potential energy surfaces along both reaction coordinates, are strongly solvent dependent. Both groups measured only lifetimes and not product distributions. Nikowa *et al.* obtain (at 1 bar and 295 K) ring closure rate constants that are about four times larger in methanol and acetonitrile than in hexane; combined with the nearly solvent independent product $F_{\mathrm{DHP}}*k_{\mathrm{rc}}$ that we deduce in Table III, this implies an equally large compensating solvent dependence of the partitioning constant $F_{\mathrm{DHP}}$ which, while possible, seems fortuitous. Our own data and model suffer from the same difficulty, although to a somewhat smaller extent; while our values for $k_{\mathrm{rc}}$ are not very precise, the variations among solvents do seem to be outside the experimental uncertainties. Possibly other aspects of the kinetic scheme outlined in eqs 1–6, such as the presumed solvent independence of the partitioning from the twisted excited state to the *cis* and *trans* ground states, need to be reexamined. We conclude that the dominant effect of solvent polarity is on the torsional isomerization pathway, but the ring closure dynamics may also be somewhat solvent sensitive. Figure 5 summarizes, qualitatively, the hypothesized solvent polarity dependence of the excited-state potential surface.

These conclusions are qualitatively supported by the resonance Raman data, which show that polar solvents enhance both the hydrogen out-of-plane and ethylenic twisting vibrations and other lines that are best described as hydrogen rocking modes having little or no twisting component. The solvent effect on the resonance Raman intensities is, however, fairly small, and the insensitivity of the absorption spectrum to solvent further indicates that solvent polarity has only a minor effect on the initial excited-state dynamics in the Franck–Condon region. This is not surprising; even if the 90° twisted phantom state is highly polarizable and/or dipolar (recent time-resolved photocalorimetric[62] and microwave conductivity measurements[63] provide increasing support for this view, at least in the much longer-lived perpendicular state of tetraphenylethylene), the vertically excited state is still likely to be relatively nonpolar, with significant charge separation occurring only as the 90° twisted structure is approached. Thus the solvent polarity effect on the excited-state surface should become increasingly pronounced as the ethylenic twist develops.

Reference 32 presented a detailed picture of the atomic motions occurring during the first 20 fs following electronic excitation of *cis*-stilbene in cyclohexane based on the resonance Raman intensities combined with a ground-state normal mode description. A similar analysis of the present intensity data might provide a clearer picture of the differences in the initial vibrational dynamics among solvents. However, the accuracy of such a procedure relies heavily on very good ground-state normal mode coefficients, as the motion of any one atom typically involves a vector sum of contributions from a number of Raman-active normal modes.

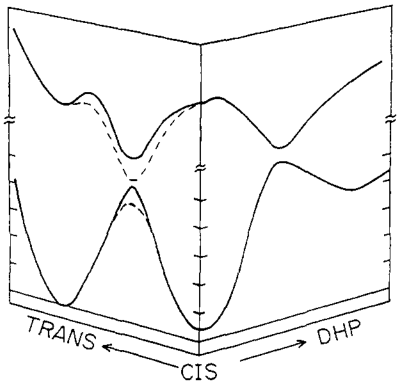

**Figure 5.** Hypothesized qualitative potential energy surfaces for the ground and first excited states of *cis*-stilbene and its two primary photoproducts in hydrocarbon solvents (solid curves) and in polar solvents (dashed curves).

For *cis*-stilbene, the best normal modes presently available are based on a rather low level of theory and have not been tested against any isotopic data, and in fact the description of the ground-state modes has been a matter of some controversy.[48,64] Also, the resonance Raman excitation profiles need to be examined in order to quantitate any preresonance contributions from the higher electronic states to the 266-nm intensities.[65,66] Therefore we believe that a more quantitative analysis of the resonance Raman intensities would be premature.

## Conclusions

We have demonstrated a strong solvent polarity effect on the quantum yields for the ultrafast *cis*-stilbene → *trans*-stilbene and *cis*-stilbene → dihydrophenanthrene photoreactions. The resonance Raman intensities are also slightly solvent dependent, suggesting that at least some of the effect on the quantum yields originates from the initial nuclear dynamics in the vertically excited Franck–Condon region. Our data, combined with literature results for the solvent-dependent excited-state lifetimes, are quantitatively consistent with a model in which the rate constant for torsional isomerization of electronically excited *cis*-stilbene is strongly dependent on solvent polarity while the rate constant for the competing ring closure reaction is less solvent dependent. This situation could arise from stabilization of a highly dipolar twisted excited state by polar solvents. However, a number of issues, particularly regarding the role of the dynamics of the solvent's dielectric relaxation on the isomerization process, remain to be sorted out.

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