

## Cisstilbene isomerization: Temperature dependence and the role of mechanical friction

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# Cis-stilbene isomerization: Temperature dependence and the role of mechanical friction

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The fluorescence decay time of *cis*-stilbene has been measured in a variety of solvents over a large temperature range. An isoviscosity Arrhenius plot in *n*-alkanes yields an activation energy of  $386 \pm 29 \text{ cm}^{-1}$ . We interpret this result as an upper limit for the *cis*-stilbene to *trans*-stilbene barrier in nonpolar solvents. Isoviscosity plots in small alcohols are nonlinear, indicating complicated behavior in this solvent type. The excited state decay times in *n*-alcohols and *n*-alkane solvents correlate well with each other when plotted as a function of chain length, *n*. We infer from this plot that macroscopic viscosity is a poor measure of the friction felt by the isomerizing species when changing solvent, and that the potential energy surface is not substantially altered between *n*-alkanes and *n*-alcohols with  $n \geq 5$ . Decay times measured in 2-propanol at 490, 475, 453, and 440 nm emission differ by no more than 90 fs, indicating that there is little or no spectral evolution during the excited state lifetime. A short component in the fluorescence anisotropy decay of *cis*-stilbene and a decrease in the excited state lifetime due to deuterium substitution for the ethylenic hydrogens are observed in both polar and nonpolar solvents. Treating DHP formation as a thermally activated process which competes with the *cis* to *trans* isomerization, we determine a range of model dependent *cis* to *trans* activation energies in alkanes of  $-300$  to  $+380 \text{ cm}^{-1}$ .

## I. INTRODUCTION

The study of the isomerization of *cis*-stilbene following electronic excitation is a useful tool for understanding how a solvent environment affects both the rate and outcome of a chemical reaction.<sup>1</sup> After ultraviolet excitation of *cis*-stilbene into its first excited singlet state, two reactions yield ground state *cis*- and *trans*-stilbene and 4*a*, 4*b* dihydrophenanthrene (DHP) believed to be in its first excited singlet state.<sup>2</sup> Although ground state *cis*-stilbene is formed, *cis*-stilbene emission has a negligible quantum yield, approximately  $10^{-4}$ .<sup>3</sup> The *cis* to *trans* isomerization is believed to involve either a small or no internal potential energy barrier. Observations of fluorescence and *cis* to *trans* photoisomerization quantum yields,<sup>4,5</sup> and the excited state lifetime of *cis*-stilbene in liquid solutions<sup>6-9</sup> suggest that *cis* to *trans* isomerization is affected by the mechanical friction of the solvent. The formation of DHP from excited *cis*-stilbene is poorly understood, but is believed to be activated<sup>2,8,10</sup> and have a branching ratio of approximately 30%<sup>11</sup> in room temperature alkanes. *Cis*-stilbene can therefore be used to study the role of mechanical friction in reactions with small or no activation energy and the competition between activated and nonactivated isomerization channels. The isomerization of *cis*-stilbene also illustrates the limitations of using the macroscopic parameter, viscosity, for describing friction in molecular processes.

There is an extensive body of work studying the role of friction in activated processes (especially isomerizations) in systems such as *trans*-stilbene,<sup>1,2</sup> diphenylbutadiene<sup>13</sup> and cyclohexane.<sup>14</sup> These investigations have been useful in testing the predictions and limitations of theoretical mod-

els based on diffusive motion.<sup>15,16</sup> They have also uncovered complicating factors such as time dependent and differential solvation of portions of the reaction coordinate,<sup>17,18</sup> frequency dependent friction,<sup>19,20</sup> and multidimensionality of the potential energy surfaces involved in the reaction.<sup>21</sup> Complications have also been found in the description of the effects of friction in simple molecular processes such as rotational reorientation<sup>22,23</sup> and diffusion.<sup>24</sup> Some of these factors will likely play a role in the complete understanding of *cis*-stilbene isomerization and testing theories, such as that proposed by Bagchi *et al.*,<sup>25,26</sup> which describe diffusive motion along a reaction coordinate which is barrierless or has a small barrier.

A quantitative description of the excited state dynamics of *cis*-stilbene will require knowledge of the shape of the excited state potential energy surface and the rate of DHP formation in polar and nonpolar environments. A useful model for the potential energy surfaces involved in these reactions is shown in Fig. 1. Optical excitation with ultraviolet light places *cis*-stilbene in the  $S_1$  state via a  $\pi^* \leftarrow \pi$  transition.<sup>27</sup> Isomerization of *cis*-stilbene to *trans*-stilbene is believed to occur by moving from the initially excited  $S_1$  state to a second excited electronic state, referred to as  $S_2$  in Fig. 1. There is substantial evidence that if there is any barrier for this  $S_1$  to  $S_2$  internal conversion it is small, however, the magnitude of the activation energy is still controversial. The  $S_2$  state is believed to have a minimum at a geometry with a  $90^\circ$  twist in the ethylenic torsion, and to rapidly internally convert to  $S_0$ , yielding both ground state *cis*- and *trans*-stilbene.<sup>1</sup>

The reaction scheme and branching ratios in Fig. 1 reproduce the steady state quantum yields of 0.55 *cis*-stilbene, 0.35 *trans*-stilbene, and 0.1 DHP (in

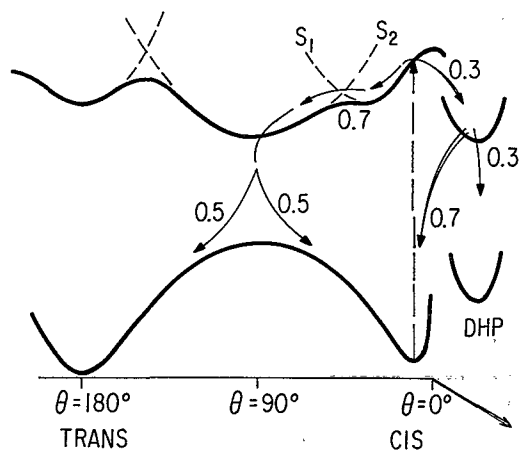


FIG. 1. Schematic minimum energy paths for stilbene isomerization in alkane solvents. The vertical dashed arrow represents the  $S_1 \leftarrow S_0$  excitation process. Room temperature branching fractions (Ref. 11) are indicated along the curved arrows. The ethylenic torsional angle,  $\theta$ , is indicated on the horizontal axis. The arrow at  $\theta=0$  points along the reaction coordinate for *cis* to DHP formation.

methylcyclohexane/isohexane mixtures).<sup>2,4</sup> The excited state of DHP yields approximately 70% ground state *cis*-stilbene and 30% ground state DHP.<sup>2,10,28</sup> Petek *et al.*<sup>11</sup> deduced the 7:3 initial branching ratio between *cis* to *trans* isomerization and *cis* to excited state DHP formation from the steady state quantum yields and the known branching ratio from the first excited state of DHP. The branching ratio between ground state *trans*- and *cis*-stilbene from the internally converting "phantom state" reached after  $S_1 \leftarrow S_0$  excitation of *trans*-stilbene is estimated to be 50:50.<sup>29</sup> The reaction scheme in Fig. 1 is appealing since it maintains a 50:50 branching ratio between *cis*-stilbene and *trans*-stilbene from the  $S_2$  intermediate state, suggesting  $S_2$  may be the same phantom state as in the isomerization of excited state *trans*-stilbene.

The short excited state lifetime for *cis*-stilbene in room temperature liquids ( $\sim 1$  ps)<sup>6-9</sup> certainly suggests that the activation energy for at least one of the two reaction channels is quite small. The observation of a 17.2 ns fluorescence lifetime for *cis*-stilbene in noble gas clusters indicates that there is a small barrier for the *cis* to *trans* isomerization in this environment.<sup>30,31</sup> Nikowa *et al.*<sup>8</sup> estimate an upper limit for the *cis* to *trans* barrier in hexane of  $0.2 kT$  at 295 K ( $41 \text{ cm}^{-1}$ ). Finally, an activation energy of  $-1.17 \text{ kcal/mol}$  ( $-409 \text{ cm}^{-1}$ ) was calculated from the temperature dependence of *cis*-stilbene fluorescence quantum yields in tetradecane and hexane using the medium enhanced barrier model.<sup>32</sup> Two complications involved in an exact determination of the barrier for *cis* to *trans* isomerization are that this process depends on solvent friction, which is a strong function of temperature, and the competing DHP formation process.

A 3.5–4.0 kcal/mol barrier is well established for the isomerization from electronically excited *trans*-stilbene in alkanes,<sup>1</sup> prompting the question: Why is there no significant barrier for the *cis* to *trans* isomerization from elec-

tronically excited *cis*-stilbene? One possible explanation is based on the large steric interactions present in *cis*-stilbene but not in *trans*-stilbene, which cause a large geometry change when the ethylenic bond order decreases upon electronic excitation.<sup>27,33,34</sup> This moves the  $S_1$  equilibrium ethylenic torsional angle closer to the  $S_2$  potential curve, possibly reducing the barrier height (as depicted in Fig. 1).

The isomerization of  $S_1$  *cis*-stilbene to DHP is poorly understood. Activation energies in nonpolar solvents of  $420 \text{ cm}^{-1}$  (Ref. 10) and  $710 \text{ cm}^{-1}$  (Ref. 8) have been reported. *Cis*-stilbene to DHP isomerization rates inferred from pressure dependence studies<sup>8</sup> are in apparent conflict with DHP quantum yields.<sup>35</sup> It is also unclear whether the branching to DHP occurs with substantial probability only immediately following excitation, or throughout the excited state lifetime. Experimental studies of *cis*-stilbene homologs<sup>11</sup> and semiempirical potential energy surface calculations<sup>36</sup> suggest that the initial motion along the potential energy surface, after electronic excitation to  $S_1$ , is in the direction of DHP formation. The semiempirical calculations<sup>36</sup> also reveal that at ethylenic torsional angles of  $30^\circ$  and  $45^\circ$ , in the range predicted for the "relaxed" excited state geometry,<sup>27,34</sup> the barrier to DHP formation increases dramatically. These conclusions have been reached with a model surface including motion along only two internal nuclear coordinates, the symmetric in-plane bend and the symmetric phenyl twist. Resonance Raman studies<sup>33</sup> and QCFF/PI force field calculations,<sup>27,33</sup> however, indicate that these internal degrees of freedom are highly mixed into many normal modes.

Although it has been established that solvent mechanical friction plays a role in determining the excited state lifetime of *cis*-stilbene, the interpretation of this finding is still incomplete. Studies include fluorescence quantum yield measurements in a variety of solvents from room temperature to liquid nitrogen temperature,<sup>4,5,10,32</sup> and more recent room temperature excited state lifetime measurements.<sup>6-9</sup> The lifetime of *cis*-stilbene in *n*-alkanes shows a weak dependence on solvent shear viscosity when viscosity is changed by changing solvent.<sup>6,7</sup> A stronger dependence of the excited state lifetime on viscosity is observed when viscosity is changed by varying pressure in a single solvent at a constant temperature.<sup>8</sup> Under these conditions the decay rate in a single solvent varies linearly with the inverse of viscosity.<sup>8</sup> The different slopes observed for *cis*-stilbene in different solvents were interpreted as resulting from a solvent dependent barrier for *cis* to *trans* isomerization.<sup>8</sup> This type of study is useful because it eliminates the variation in solvent specific factors that affect friction, which complicates studies in different solvents. However, in rotational reorientation studies, Artaki and Jonas<sup>37</sup> have shown that even in a single solvent it is necessary to change viscosity by changing pressure *under isochoric conditions* (constant volume) to use viscosity as a measure of friction. One must therefore be cautious when assuming that friction behaves linearly with viscosity in isothermal pressure dependent experiments.

Our goals in this study are to determine the size of any barrier which may exist along the *cis* to *trans* isomerization

coordinate and learn how the potential energy surface for both *cis* to *trans* isomerization and DHP formation depend on solvent polarity. We have measured the temperature dependence of the fluorescence decay time in alcohols and alkanes both within a single solvent and under isoviscosity conditions by changing both solvent and temperature. Measurements of the deuterium isotope effect in a polar solvent and the fluorescence anisotropy decay in a nonpolar solvent are used to investigate the reaction coordinate and the effects of solvent polarity. A strong correlation between fluorescence decay time and solvent chain length unifies long chain *n*-alkane and *n*-alcohol data and suggests that solvent polarity has little effect on the potential energy surfaces for *cis* to *trans* isomerization for large chain length, *n*, and that care must be taken when trying to understand the role of friction in molecular reactions in terms of a macroscopic quantity such as viscosity.

## II. EXPERIMENT

### A. Apparatus

The excited state dynamics of *cis*-stilbene are monitored using time resolved fluorescence upconversion. The experimental apparatus has been described in detail elsewhere<sup>6,38</sup> and will only be summarized here with mention of a few modifications. A dual jet dye laser was synchronously pumped by the second harmonic of a mode-locked Quantronix Nd:YAG laser. The dye laser output was amplified in a system pumped by an Oxford copper vapor laser. Amplified pulses for most of the experiments were between 0.5 and 0.7 ps in duration with roughly 3  $\mu\text{J}$  per pulse at 6 kHz. The dyes used in the laser were sulforhodamine 640 for the gain and DQTCI as absorber, operating nominally at 634 nm. The second harmonic of the dye laser, at 317 nm, was used to excite *cis*-stilbene. The remaining fundamental traversed a variable delay line

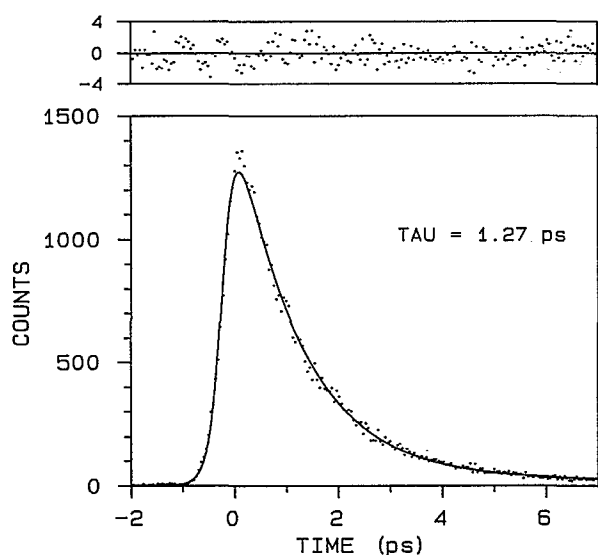


FIG. 2. Fluorescence decay curve for *cis*-stilbene in decane at 20°C. Excitation is at 316 nm and emission is at 475 nm. The solid line is a nonlinear least squares fit, and the residuals are shown above.

TABLE I. *Cis*-stilbene fluorescence decay times. Best fits to single exponential decay.

(a) Polar solvents				
Solvent	Temp.	$\lambda_{\text{emission}}$	$\eta$	Decay time
Methanol	20.0 deg. C	465 nm	0.59 cp	0.50±0.04 ps
2-Propanol	20.0 deg. C	440 nm	2.38 cp	0.83±0.05 ps
2-Propanol	20.0 deg. C	453 nm	2.38 cp	0.78±0.03 ps
2-Propanol	20.0 deg. C	475 nm	2.38 cp	0.80±0.04 ps
2-Propanol	20.0 deg. C	490 nm	2.38 cp	0.74±0.03 ps
<i>n</i> -Pentanol	20.0 deg. C	475 nm	4.18 cp	0.94±0.05 ps
Ethanol	-9.0 deg. C	475 nm	2.36 cp	0.74±0.04 ps
Pentanol	38.0 deg. C	475 nm	2.42 cp	0.89±0.04 ps
Methanol	-21.5 deg. C	475 nm	1.20 cp	0.63±0.04 ps
2-Propanol	45.0 deg. C	475 nm	1.17 cp	0.64±0.04 ps
<i>n</i> -Butanol	58.0 deg. C	475 nm	1.20 cp	0.67±0.03 ps
2-Propanol	38.5 deg. C	475 nm	1.39 cp	0.63±0.03 ps
2-Propanol	8.0 deg. C	475 nm	3.50 cp	0.87±0.03 ps
Acetonitrile	20.0 deg. C	475 nm	0.38 cp	0.38±0.03 ps
DMSO	20.0 deg. C	475 nm	2.20 cp	0.63±0.03 ps
<i>D<sub>2</sub></i> - <i>cis</i> -Stilbene				
2-Propanol	20.0 deg. C	490 nm	2.38 cp	0.38±0.04 ps
2-Propanol	20.0 deg. C	475 nm	2.38 cp	0.86±0.03 ps
(b) Nonpolar solvents				
Solvent	Temp.	$\lambda_{\text{emission}}$	$\eta$	Decay time
Decane	20.0 deg. C	475 nm	0.92 cp	1.27±0.05 ps
Dodecane	23.0 deg. C	475 nm	1.45 cp	1.35±0.06 ps
Cyclohexane	20.0 deg. C	450 nm	0.97 cp	1.53±0.06 ps
Octane	-7.0 deg. C	475 nm	0.78 cp	1.58±0.04 ps
Decane	31.0 deg. C	450 nm	0.78 cp	1.23±0.04 ps
Dodecane	64.0 deg. C	475 nm	0.78 cp	1.02±0.03 ps
Tetradecane	87.0 deg. C	475 nm	0.78 cp	0.92±0.05 ps
Tetradecane	54.0 deg. C	475 nm	1.26 cp	1.08±0.05 ps

and was then mixed with the *cis*-stilbene fluorescence in a 1 mm BBO crystal. The upconverted light was separated from the other light using a prism, directed into a 0.3 m single monochromator, and detected with a solar blind photomultiplier tube. The signal intensity was determined by single photon counting techniques with the count rate kept below 5% of the amplified dye laser repetition rate.

A few of the data points were obtained with a slightly modified dye laser<sup>39</sup> generating nearly transform limited pulses between 90 and 110 fs in duration. A fold mirror, between the prisms used for group velocity dispersion compensation, was removed and the prism separation was set to ca. 26 cm. The dyes used for generating the short pulses are kiton red (2 mM) and DODCI, and the laser operated at approximately 632 nm. The pump power was set at approximately 820 mW and the focal lengths of all resonator mirrors were the same as used previously.<sup>40</sup> The pulses, which were broadened to 600 fs by the amplifier, were compressed down to 200 fs using a pair of quartz prisms. Compression back to 100 fs should be possible with more dispersive prisms. A typical data set, obtained with the modified apparatus (for *cis*-stilbene in decane), is shown in Fig. 2. The instrument response function used for deconvolution has a F.W.H.M. of 420 fs and the *cis*-stilbene fluorescence decay time was determined to be 1.27 ± 0.05 ps [see Table I(b)].

The fluorescence decay curves are fit to a biexponential form convoluted with a simulated instrument response

function, the width of which was varied to fit the rising edge.<sup>6</sup> The first component of the fit is assigned to the loss of excited state *cis*-stilbene. We attribute the second component of the fit to the decay of a small amount of *trans*-stilbene impurity also excited by the second harmonic pulse. The *trans*-stilbene contribution is small, typically 1%–2%, at the excitation and emission wavelengths used in this study. The *cis*-stilbene lifetime extracted from the fit is insensitive to the exact lifetime used to fit the *trans*-stilbene component. Attempts to fit the data with an increasing exponential component (on the rising edge) were unsuccessful.

No polarizers were used for the simple lifetime measurements. The observed signal is therefore the parallel component of the anisotropy. Both experiment and simulations were used to show that this has a negligible effect on the extracted *cis*-stilbene lifetimes.<sup>6</sup> For the anisotropy experiment, polarizers were used in the excitation beam path and for analyzing the fluorescence. The short lifetime of *cis*-stilbene and the overlapping emission of *trans*-stilbene complicates the fluorescence anisotropy decay measurements. As *cis*-stilbene decays, its contribution to the anisotropy is reduced and is soon overwhelmed by the *trans*-stilbene contribution. The effects of overlapping emission, from two or more species, on the fluorescence anisotropy have been discussed by Chang *et al.*<sup>41</sup> (see esp. Fig. 6 of Ref. 41). We have minimized this problem by using well purified *cis*-stilbene samples and by upconverting emission at 450 nm, where *cis*-stilbene fluoresces strongly,<sup>3</sup> but *trans*-stilbene does not.

The temperature range covered in this study is –22.5 to 87 °C. For the majority of the experiments the temperature was maintained using one of two Nestlab circulators. For temperatures below –9 °C the sample was flowed through a stainless steel coil immersed in an acetone/dry-ice bath. For all temperatures below 10 °C dry nitrogen gas was blown over the sample cell and the reservoir to avoid condensation of water. In all experiments the sample was flowed, and the temperature measured directly after the interaction region.

## B. Materials

*Cis*-stilbene was obtained from Aldrich and purified using radial chromatography with pentane as the eluent. *Cis*-stilbene-D<sub>2</sub> was synthesized from D<sub>2</sub> (Matheson c.p. grade) and diphenylacetylene as described previously.<sup>6</sup> All solvents were either Baker spectrophotometric grade, Burdick and Jackson high purity solvents, or the purest available from Aldrich and were used without further purification.

## III. RESULTS

### A. Lifetime measurements

A summary of all the fluorescence lifetime data is presented in Tables I(a) and I(b). The tabulated viscosity values were calculated either by using empirical formulas<sup>42</sup> or by interpolation using data in Ref. 43. We first observe that decay times for *cis*-stilbene in 2-propanol at room tem-

perature obtained at emission wavelengths of 440, 453, 475, and 490 nm, are roughly the same, with a statistically weighted average of  $0.78 \pm 0.02$  ps. These lifetimes also agree with our previous value obtained at 400 nm.<sup>6</sup> A longer decay time, measured at 430 nm emission in our previous study,<sup>6</sup> is probably the result of the shorter excitation wavelength used in that study (292 vs 317 nm). These data strongly suggest that there is little or no change in the position and shape of the emission spectrum on the time scale of the excited state lifetime. This is consistent with the findings of spectral calculations<sup>34</sup> that the emitting excited state is displaced from the ground state geometry a maximum of roughly 37° along the ethylenic torsion. If emission were originating from the 90° twisted intermediate, or phantom state, an extremely large redshift in the spectrum associated with nuclear motion on the timescale of the fluorescence decay would be expected.<sup>34</sup>

Another significant observation from Table I is that cyclohexane and decane, which have nearly the same viscosity, yield quite different *cis*-stilbene lifetimes. Although a change in the potential energy surface due to solvent polarity has been previously used to explain the difference in the decay times in polar and nonpolar solvents of the same viscosity (2-propanol and tetradecane)<sup>6</sup> our present results indicate that some other factors must be contributing to the decay rate. Our measured decay time of 1.53 ps in cyclohexane is in good agreement with the  $1.51 \pm 0.26$  ps decay time measured by Rice *et al.*,<sup>9</sup> using transient absorption, at a probe wavelength of 660 nm. Their transient absorption decay times measured in cyclohexane have a strong probe wavelength dependence varying from 1.23 ps at 590 nm to 2.07 ps at 640 nm with an average of  $1.83 \pm 0.4$  ps.<sup>9</sup>

Given the short lifetime and lack of a substantial barrier for *cis* to *trans* isomerization it is important to establish that our decay times represent a true population decay. We have established this connection for *cis*-stilbene in alkane solvents using the remarkable agreement of decay times obtained by transient fluorescence<sup>6</sup> and absorption<sup>7</sup> for *cis*-stilbene in hexane. Our 0.50 ps fluorescence lifetime for *cis*-stilbene in methanol is in excellent agreement with recent transient absorption decay times in this solvent<sup>8,9,44</sup> suggesting that both techniques measure population decay in polar as well as nonpolar solvents.

The decay time of *cis*-stilbene-D<sub>2</sub> in 2-propanol was measured to complement previous results in tetradecane and investigate any differences in the effect of polar and nonpolar solvents. An increase in decay time of roughly 74 fs or  $9.5\% \pm 4\%$  was observed upon deuteration of the ethylenic hydrogens. In tetradecane, deuterium substitution causes a  $24\% \pm 13\%$  increase in decay time.<sup>6</sup> This increase in lifetime upon deuteration may result from either a change in rate of the *cis* to *trans* or the *cis* to DHP isomerization process, or both. Because of the large uncertainty of our tetradecane result, we cannot determine whether the isotope effect is different from that in 2-propanol. In tetradecane, a small increase in the fluorescence quantum yield for *cis*-stilbene-D<sub>2</sub> was observed recently by Saltiel *et al.*<sup>32</sup> The average of fluorescence

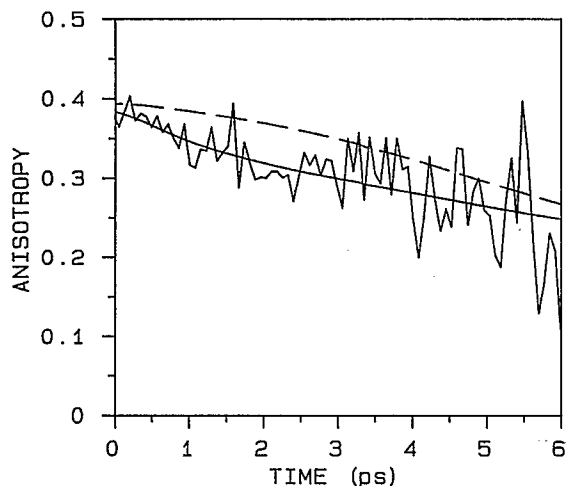


FIG. 3. Fluorescence anisotropy decay of *cis*-stilbene in decane at 31 °C. The smooth lines are anisotropies calculated from nonlinear least squares fits to the experimental parallel and perpendicular decays (Ref. 47). The anisotropy for the solid curve has two components, one with a 1.06 ps lifetime and an amplitude of 0.07 and the second with a 35 ps lifetime and an amplitude of 0.33. For the dashed curve, the anisotropy has only one component with an amplitude of 0.40 and a lifetime of 35 ps, corresponding roughly to overall molecular tumbling. For both calculated curves, the magic angle decay was fit to a double exponential with the second lifetime fixed to 103 ps, the fluorescence lifetime of *trans*-stilbene in decane.

quantum yields at four temperatures<sup>32</sup> increases  $9.5\% \pm 3\%$  on deuteration of the ethylenic hydrogens, in very good agreement with the percent change in lifetime observed in 2-propanol. However, Saltiel *et al.*<sup>32</sup> found no noticeable isotope effect on the fluorescence quantum yields of *cis*-stilbene in hexane.

Decay times for *cis*-stilbene in dimethyl sulfoxide (DMSO) and acetonitrile were measured to determine if solvation dynamics plays an important role in the isomerization process. The fluorescence decay time in DMSO is more than 140 fs shorter than the average decay time in 2-propanol (0.78 ps), which has roughly the same viscosity but a much slower solvation time.<sup>45</sup> The decay time in acetonitrile, which has a large amplitude 70 fs solvation relaxation time,<sup>46</sup> is very short, 380 fs, and is in excellent agreement with the value observed by Nikowa *et al.*<sup>8</sup> using transient absorption.

In our previous work we observed a small amplitude picosecond component in the fluorescence anisotropy decay of *cis*-stilbene in 2-propanol.<sup>6</sup> We have performed the same experiment for *cis*-stilbene in decane, to determine if the presence of a fast component depends on solvent polarity. The experimental anisotropy is plotted in Fig. 3. The parallel and perpendicular decays consist of 26 scans each and have peak counts of 2900 and 1000, respectively. Also plotted in Fig. 3 are anisotropy decays with and without a fast component, which were calculated from least squares fits to the parallel and perpendicular decays.<sup>6,47</sup> In the fitting procedure the magic angle decay is fit to a double exponential, with the lifetime of the second component fixed at 103 ps, the fluorescence lifetime of *trans*-stilbene in

decane.<sup>48</sup> The best fit curve ( $\chi^2_v = 1.38$ ) has  $R(0) = 0.40$  and a fast component with a lifetime of roughly 1.0 ps and an amplitude of 0.07. This agrees well with the 2-propanol result<sup>6</sup> in which the fast component also has an amplitude of 0.07 and the same lifetime within experimental error. The dependence of the small amplitude picosecond anisotropy component on polarity is apparently slight.

## B. Temperature dependence

Some information about the shape of the potential energy surface, in particular, the activation energy, is required for quantitative calculations of the *cis* to *trans* isomerization rate, especially for the application of stochastic theories such as that proposed by Bagchi, Fleming, and Oxtoby (BFO)<sup>25,26</sup> or the Kramers equation.<sup>15</sup> Arrhenius plots of  $\ln(k)$  vs  $1/T$  (where  $k$  is the rate and  $T$  is the temperature) are the standard technique for determination of activation energies. In a reaction which depends on friction, the strong temperature dependence of the solvent friction will affect the observed decay times, complicating the interpretation of Arrhenius plots in a single solvent. This difficulty is partially circumvented by isoviscosity Arrhenius plots<sup>49</sup> where viscosity is kept constant by simultaneously changing solvent and temperature. Ideally, we would like to keep the friction experienced by the reacting species constant as temperature is varied. Unfortunately, we have as yet no direct technique for measuring the appropriate friction. Nevertheless, the isoviscosity technique has been used successfully to obtain the barrier to isomerization for excited state *trans*-stilbene.<sup>49</sup>

Isoviscosity Arrhenius plots for both alkane and alcohol solvents are displayed in Figs. 4(a) and 4(b), respectively. Along with these data are plotted the single solvent Arrhenius plots for *cis*-stilbene in 2-propanol and tetradecane. The single solvent curves are obviously not isoviscosity since viscosity is a strong function of temperature. The isoviscosity data for the alkanes was obtained for a viscosity of 0.78 cP over temperatures ranging from  $-7$  °C in octane to 87 °C in tetradecane. The alkane isoviscosity Arrhenius plot is linear within error and a least squares fit yields an activation energy of  $386 \pm 29$  cm<sup>-1</sup>. We suggest that this activation energy be considered an upper bound for the *cis* to *trans* isomerization in nonpolar solvents for two reasons. First, in the excited state of *cis*-stilbene there is a second reaction channel which leads to the formation of DHP and has a barrier believed to be greater than 400 cm<sup>-1</sup>.<sup>8,10</sup> This would tend to increase the activation energy determined in this type of experiment. Second, although we are measuring lifetimes under isoviscosity conditions, the friction experienced probably decreases with the increasing length of the alkane chain due to increasing free volume and frequency dependent friction effects.<sup>19,20</sup> As solvent chain length is increased, there is an increase in the contribution to the viscosity from solvent modes which are too slow to contribute to the friction for *cis* to *trans* isomerization. Both frequency dependent friction and free volume effects would tend to increase the experimentally determined activation energy beyond its true value.

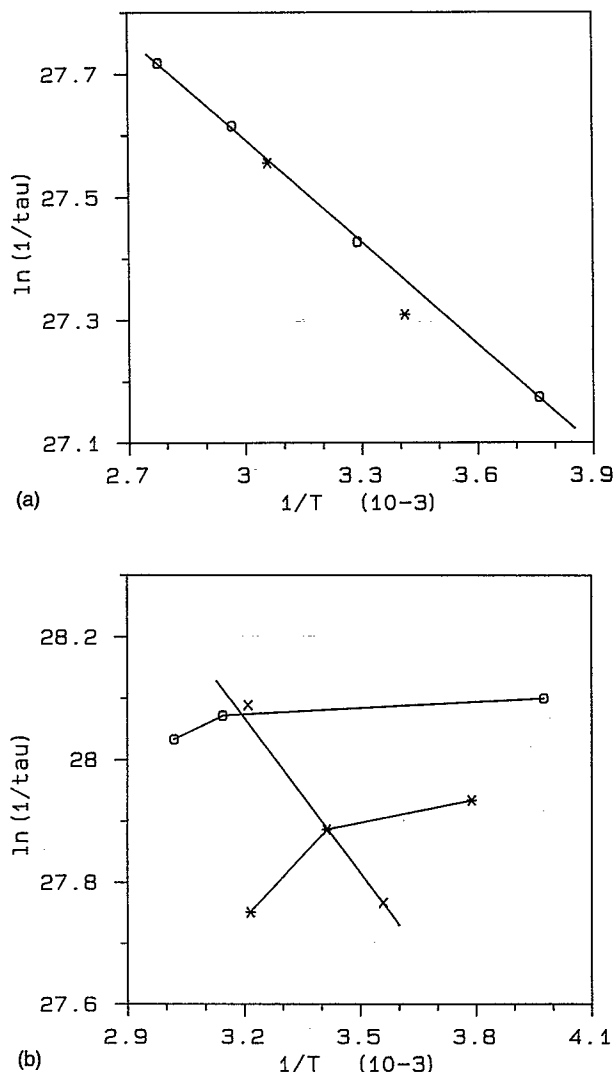


FIG. 4. Isoviscosity Arrhenius plots.  $\ln(1/\tau)$  vs  $1/T$  (a) In the *n*-alkanes.  $\circ$ : octane, decane, dodecane, and tetradecane at a viscosity of 0.78 cp. The slope yields an activation energy of  $386 \pm 29 \text{ cm}^{-1}$ .  $*$ : *cis*-stilbene in tetradecane (not isoviscosity), shown for comparison. (b) In alcohols.  $\circ$ : methanol, 2-propanol, and *n*-butanol at 1.2 cp.  $*$ : ethanol, 2-propanol, and *n*-pentanol at 2.38 cp.  $\times$ : *cis*-stilbene in 2-propanol (not isoviscosity), shown for comparison.

Isoviscosity plots in alcohols were constructed at two viscosities, 1.2 and 2.36 cP, and display peculiar behavior. They appear flat for the smallest alcohols used and then curve down, in the direction of negative activation energy, as the chain length is increased. The curvature may originate from a changing relationship between friction and viscosity, a polarity dependence of either isomerization, or some combination of these effects.

The single-solvent Arrhenius plots are linear within error in both 2-propanol and tetradecane. The slopes of these lines yield activation energies of  $587 \pm 84 \text{ cm}^{-1}$  in 2-propanol and  $435 \pm 92 \text{ cm}^{-1}$  in tetradecane. The temperature dependence of the *cis*-stilbene lifetime,  $\tau$ , observed in tetradecane can be indirectly compared with fluorescence quantum yields,  $\phi_F$ , determined by Saltiel *et al.*<sup>32</sup> over a similar temperature range. A direct comparison is not pos-

sible because  $\phi_F$  and  $\tau$  were not determined at the same temperatures. We assume the quantum yield and lifetime can be related by,<sup>50</sup>

$$\phi_F = k_F \tau \quad (1)$$

as for single exponential decay, and that the radiative rate,  $k_F$ , is independent of temperature. From the quantum yields we determine an activation energy of  $674 \text{ cm}^{-1}$ , in disagreement with our result. Actually, the radiative rate,  $k_F$ , is expected to decrease with increasing temperature due to the decreasing index of refraction<sup>50</sup> and the activation energy we obtain from the quantum yields is therefore an overestimate.

#### IV. DISCUSSION

Any model of the photophysics of *cis*-stilbene must take account of two processes which lead to excited state population decay, the *cis* to *trans* and *cis* to DHP isomerizations. To calculate lifetimes we need a model for the kinetics, at least a crude model for the excited state surface appropriate to both processes, and a knowledge of how this surface is altered by different solvents. We also need to know to what degree each process is affected by friction and how to calculate the friction appropriate for each process in terms of measurable quantities like viscosity, solvent shape and free volume. Modeling the friction also requires a knowledge of the molecular motions involved in the isomerizations.<sup>6</sup>

For our calculations we assume a quasiequilibrium state (or geometry) is rapidly reached after excitation and that the population of this state is monitored in our experiments. From this geometry the two isomerization reactions compete. We assume the *cis* to *trans* reaction takes place along a path with little or no barrier<sup>8,30,32</sup> and is influenced by solvent friction. It is assumed that the *cis* to DHP reaction is activated [barrier between  $420 \text{ cm}^{-1}$  (Ref. 10) and  $710 \text{ cm}^{-1}$  (Ref. 8)] and relatively unaffected by solvent friction. Although other reaction schemes have been suggested,<sup>11</sup> this is the simplest scheme which seems to capture the essential photophysics.

In the context of this reaction scheme, it appears, at first glance, that the activated formation of DHP would not compete effectively with barrierless *cis* to *trans* isomerization. To our knowledge, there has been no theoretical treatment of the competition between an activated process which is unaffected by friction and a barrierless process which is impeded by friction. Qualitatively, we expect that frictional forces will keep excited *cis*-stilbene at a nuclear geometry where DHP formation is still possible. Besides providing friction, collisions with the solvent also supply the energy needed to activate DHP formation. Based on this model, we expect little or no DHP formation in isolated *cis*-stilbene.

We now turn to a discussion of solvent-induced changes in the potential energy surface and the frictional forces exerted by individual solvents.



### A. Solvent dependence of friction and the potential energy surface

There is evidence suggesting that the excited state potential energy surface of *cis*-stilbene is solvent dependent. For example, the decay rate for *cis*-stilbene in 2-propanol is almost twice as fast as that in tetradecane, which has the same viscosity. Nikowa *et al.*<sup>8</sup> inferred rates of DHP formation approximately three times faster in methanol and acetonitrile than in *n*-alkanes of similar viscosities and suggested that the potential energy surface for the *cis* to *trans* reaction is changing from polar to nonpolar solvents and even between different *n*-alkanes. The difference in lifetimes observed in polar and nonpolar solvents of the same viscosity *may* result from an alteration in the potential energy surface along one or both of the reaction coordinates. However, we believe it is unlikely that the difference in decay times observed in decane and cyclohexane [Table I(b)], which have nearly the same viscosity, has the same origin. As an alternative, we will attempt to explain our results in terms of the solvent specific relationship between friction and viscosity.

Nikowa *et al.*<sup>8</sup> have shown that the excited state decay rate varies linearly with the inverse of the viscosity in a single solvent when the viscosity is varied by changing the pressure at constant temperature. That is, the decay rates,  $k_{nr}$  obtained in a single solvent empirically fit the functional form,<sup>8</sup>

$$k_{nr} = b + A/\eta \quad (2)$$

when viscosity was changed by varying pressure. This simple result contrasts with the more complicated behavior and weak viscosity dependence of the decay rate when viscosity is varied by changing solvent.<sup>6,7</sup> The different slopes,  $A$ , obtained for different solvents were interpreted as a result of changes in the potential energy surface for *cis* to *trans* isomerization and the nonzero intercepts,  $b$ , at infinite viscosity were attributed to the rate of DHP formation (assumed to be viscosity independent).<sup>8</sup> Their study established that the data can be explained without a fractional power dependence of the rate on the inverse of viscosity. However, their interpretation of the varying slopes in terms of a change in the potential energy surface is not unique, as shown below.

An alternative interpretation is that the slope indicates the relationship between macroscopic viscosity and the friction experienced by isomerizing *cis*-stilbene. We suggest that data obeying Eq. (2) can be described more generally by the equation

$$k_{nr} = b + B/\zeta, \quad (3)$$

where  $\zeta$  is the friction. If we assume that friction is proportional to viscosity in a single solvent and that the proportionality constant is independent of pressure, then Eq. (2) follows from Eq. (3) and  $A = B(\eta/\zeta)$ . Even if the constant  $B$  appearing in Eq. (3) is solvent independent (e.g., no change in the potential energy surface for *cis* to *trans* isomerization), the constant  $A$  in Eq. (2) can be solvent dependent because the proportionality between friction and viscosity can change from solvent to solvent. If

$B$  is solvent independent, then for a given viscosity there is less friction in solvents with larger values of  $A$ . For barrierless processes, nonradiative rates inversely proportional to friction are predicted by all one-dimensional "instantaneous death" models and as a limiting case of more general models.<sup>26</sup> In the study of Nikowa *et al.*<sup>8</sup>  $A$  (measured in  $10^{11} \text{ s}^{-1} \text{ cp}$ ) increases from 1.6 in *n*-pentane to 3.6 in *n*-nonane, and becomes quite large, 6.3 and 6.4, in acetonitrile and methanol, respectively. These trends are consistent with those expected from an increase in free volume with chain length,<sup>4,5</sup> frequency dependent friction,<sup>20</sup> and hydrogen bonding. Hydrogen bonding, which has a profound effect on the macroscopic viscosity, is likely to have a reduced effect on the isomerization of *cis*-stilbene, possibly explaining the relatively large value of  $A$  in methanol.<sup>8</sup> Within the framework just discussed, we suggest that the difference in decay times between cyclohexane and decane, which have the same viscosity but very different shapes, results from a difference in the friction experienced by isomerizing *cis*-stilbene in these two solvents.

Our interpretation of the pressure dependence studies is supported by measurements of rotational reorientation times of *trans*-stilbene in alkane and alcohol solvents.<sup>22</sup> The solvent dependence of  $A$  in Eq. (2) is analogous to the solvent dependent slopes in plots of rotational reorientation rate vs  $T/\eta$ , where changes in an internal potential energy surface are not relevant. For each *n*-alkane, the rotational reorientation rate varies linearly with  $T/\eta$ , but the slopes increase with increasing chain length,  $n$ .<sup>22,51</sup> This is the same trend in slopes observed for *cis*-stilbene excited state decay rates as a function of  $1/\eta$ .<sup>8</sup> The most straightforward explanation for the reorientation data, is that the proportionality between friction and viscosity changes as the solvent is changed. The slopes for the rotational reorientation rates<sup>22</sup> change more gradually with chain length than the slopes for *cis*-stilbene nonradiative rates. This is reasonable, since rotational reorientation is slower, sweeps out a larger volume, and samples more of the bulk properties of the solvent. The analogy between *trans*-stilbene rotational reorientation and the *cis*-stilbene excited state decay rates also extends to a comparison between polar and nonpolar solvents. The rates for both processes are larger in alcohol solvents than in alkane solvents of equal viscosity.<sup>52</sup>

The implication of the foregoing discussion is that the *cis*-stilbene potential surface varies little from alkane to alkane. Can this conclusion be extended to polar solvents? A plot of our room temperature decay times as a function of viscosity (Fig. 5) reveals little correlation between polar and nonpolar solvents or between linear alkanes and cyclohexane. There appears to be a roughly linear relationship between the decay times in the short-chain alcohols. However, extrapolation of this line to the viscosity of decanol predicts a decay time of roughly 2.4 ps for *cis*-stilbene in this solvent, nearly twice the experimental value.

A most intriguing observation is that the lifetimes for *cis*-stilbene in decane and decanol (decanol at 400 nm emission<sup>6</sup>) are identical (1.27 ps). This equality is surely coincidental, but suggests that the environment surround-



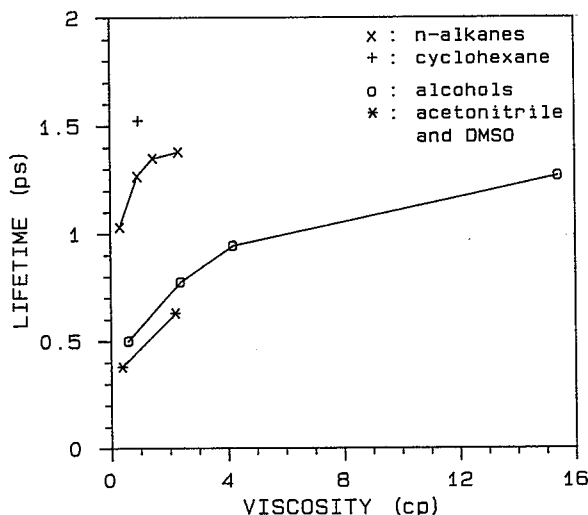


FIG. 5. *Cis*-stilbene excited state decay time at room temperature as a function of viscosity in various solvents.

ing *cis*-stilbene in these two solvents may be similar. We investigated this possibility by plotting lifetime as a function of chain length for linear alkanes and alcohols in Fig. 6. A startling degree of correlation between all the data is revealed. Included in Fig. 6 are our present and previous<sup>6</sup> fluorescence decay results, and the absorption decay times of Abrash *et al.*,<sup>7</sup> Rice *et al.*,<sup>9</sup> and Nikowa *et al.*<sup>8</sup> Note that the gas phase result of Green and Farrow<sup>53</sup> coincides approximately with the zero chain length intercept on this graph. In addition to the agreement of the decane and decanol lifetimes, the decay times in pentanol ( $0.94 \pm 0.05$  ps), *n*-pentane ( $0.99 \pm 0.04$  ps),<sup>8</sup> and even isopentane ( $0.99 \pm 0.07$  ps)<sup>7</sup> are similar and in general the alcohol and alkane curves overlap well. This lends us to suggest that

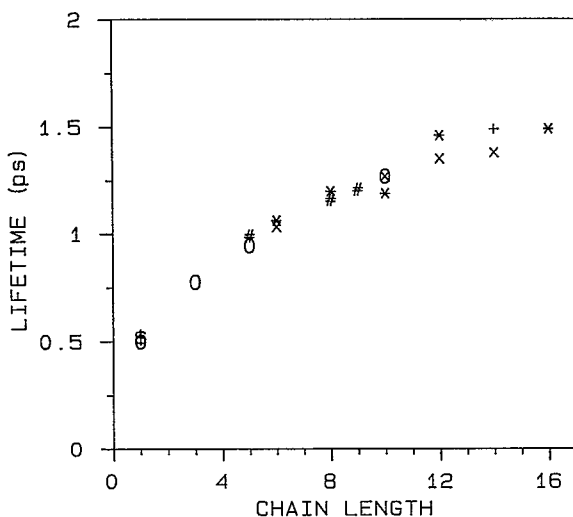


FIG. 6. *Cis*-stilbene excited state decay time at room temperature as a function of solvent chain length (number of carbon atoms). *n*-alkanes, X: This study and Ref. 6, \*: Ref. 7, +: Ref. 9, #: Ref. 8. *n*-alcohols and 2-propanol, O: This study and Ref. 6, \$: Ref. 8.

*cis*-stilbene may experience a similar environment in *n*-alkanes and *n*-alcohols of similar chain length—at least for  $n \geq 5$ .

We draw two inferences from this presentation of the data. First Fig. 6 suggests the parameters that determine friction for *cis* to *trans* isomerization are not well reflected in the macroscopic viscosity of the solvent. It seems that the local environment or the microscopic friction nature of the solvent is determining the mechanical friction and therefore the reaction rate. A second and equally important conclusion that can be drawn from Fig. 6 is that the potential energy surface is the same for *cis*-stilbene in long chain *n*-alcohols ( $n \geq 5$ ) and their *n*-alkane counterparts. If, in polar solvents, *cis*-stilbene is exposed only to the nonpolar part of the solvent molecule, it becomes plausible that the environment of *cis*-stilbene in long chain alcohols is similar to that in alkanes of equal length. This explanation is supported by the low solubility of *cis*-stilbene in water,<sup>54</sup> ethylene glycol, and glycerol. In the smaller alcohols, the shorter chain length would not effectively isolate *cis*-stilbene from the polar group and the barriers for DHP formation or *cis* to *trans* isomerization may be altered.

Solvent polarity is believed to drastically reduce the barrier for *trans* to *cis* isomerization.<sup>1</sup> If the potential energy surface for *cis* to *trans* isomerization is not strongly dependent on solvent polarity, it seems reasonable to ask why. One explanation is that steric interactions force the  $S_1$  minimum into the vicinity of the curve crossing with  $S_2$ . Because the local slope of the  $S_1$  curve is small near the  $S_1$  minimum, changes in the  $S_2$  potential would have only a small effect on the barrier. A second possible reason for the reduced sensitivity to solvent polarity of the *cis* to *trans* barrier is that most solvents cannot rearrange and solvate the transient species during the short lifetime of excited *cis*-stilbene. Dynamic solvent effects are believed to play a role in determining the effective barrier for *trans* to *cis* isomerization in polar solvents<sup>1,17</sup> and are believed to cause the complicated behavior of *trans*-stilbene isoviscosity Arrhenius plots.<sup>17</sup> The *cis*-stilbene excited state lifetime may be too short for these processes to have a substantial effect in all but the smallest alcohol solvents, acetonitrile, and DMSO.

Although others have suggested that the barrier to DHP formation is reduced in small polar solvents,<sup>8</sup> there are some difficulties for this interpretation. From the intercepts obtained in their fits to Eq. (2) Nikowa *et al.*<sup>8</sup> infer that the rate of DHP formation is approximately three times faster in methanol than in *n*-alkanes. This apparently conflicts with Rodier *et al.*'s<sup>35</sup> inference from measured photocyclization (DHP formation) yields that the rate is at least a factor of 2 greater in cyclohexane than in methanol. We assume for discussion that the yield of excited DHP is related to the rate of DHP formation by

$$\phi_{\text{DHP}} = k_{\text{DHP}} \tau. \quad (4)$$

If the rate of DHP formation is three times greater in methanol than in cyclohexane, then using our excited state lifetimes we predict the same DHP yield in the two solvents, in disagreement with the experimental yields.<sup>35</sup> Ni-

kowa *et al.*<sup>8</sup> determined the rate of DHP formation in methanol by extrapolating the rate of *cis*-stilbene population decay, obtained with viscosities varying only by a factor of 3, to the limit  $1/\eta \rightarrow 0$  (i.e., infinite viscosity)<sup>55</sup> so that the DHP formation rate obtained by this method may be quite uncertain.

If we assume instead that the rate of DHP formation in methanol and cyclohexane is roughly the same, then the difference in the directly measured DHP yields<sup>35</sup> can be simply explained as a result of the difference in *cis*-stilbene lifetimes. Writing the yield of DHP in cyclohexane as  $\phi_{\text{DHP}}^c$  and in methanol as  $\phi_{\text{DHP}}^m$  and using Eq. (4) we obtain the ratio of the two yields

$$\phi_{\text{DHP}}^c/\phi_{\text{DHP}}^m = \tau^c/\tau^m = 1.525/0.50 \approx 3,$$

in agreement with Rodier *et al.*'s<sup>35</sup> measurement. The difference in lifetimes reported both here and elsewhere<sup>9</sup> could then be attributed to a change in the rate of *cis* to *trans* isomerization. A change in the *cis* to *trans* rate resulting from increased friction in cyclohexane over that in methanol is likely since the viscosity is larger in cyclohexane, the value of  $A$  in Eq. (2) is smaller (more friction per viscosity) in alkanes than in methanol,<sup>8</sup> and cyclohexane seems to have greater friction than alkanes of the same viscosity (e.g., see Fig. 5). The *cis* to *trans* activation energy may also be altered in methanol and other solvents with fast solvation times. Within our kinetic scheme, however, we can explain both the relative yields of DHP<sup>35</sup> and the *cis*-stilbene decay times in both polar and nonpolar solvents without assuming changes in the potential energy surface for either DHP formation or *cis* to *trans* isomerization.

## B. Friction from solvent parameters and molecular motion

A description of *cis*-stilbene excited state lifetimes requires a method for calculating the friction appropriate for the *cis* to *trans* isomerization from measurable solvent parameters. It would be useful to find a parameter more general than solvent chain length that correlates lifetimes observed in solvents of different shape and type. Since solvent free volume is often used to parametrize friction and viscosity<sup>56</sup> we have looked for a correlation of the *cis*-stilbene excited state lifetimes with this variable. For this discussion, molar free volume ( $V_f$ ), is defined as

$$V_f = V_T - V_w, \quad (5)$$

where  $V_T$  is the molar volume of the solvent and  $V_w$  is the van der Waals volume per mole.  $V_f/N_a$ , where  $N_a$  is Avogadro's number, is the free volume per molecule. The van der Waals volumes were either obtained from McGowen and Mellors<sup>57</sup> or calculated using the formulas of Bondi.<sup>58</sup> The correlation observed between *n*-alkanes and *n*-alcohols is as good as in the plot of lifetime vs chain length (Fig. 6). This correlation, however, does not necessarily imply a trivial relationship between free volume and friction. The decay time in cyclohexane does not correlate well with the other data suggesting that the trend in the relationship between free volume and solvent friction

observed in *n*-alcohols and *n*-alkanes does not work for a solvent molecule of very different molecular shape or structure.

The friction experienced in the *cis* to *trans* isomerization and the time scale of this motion will, of course, depend upon the size and degree of the nuclear rearrangements which occur. From the fluorescence anisotropy decay in 2-propanol<sup>6</sup> and in decane, which occurs on the same time scale as the excited state lifetime, we infer that there is some large amplitude nuclear motion associated with one of the two isomerization processes—probably the *cis* to *trans* isomerization. In a study of the absorption and emission spectra of *cis*-stilbene<sup>34</sup> we suggested that the *cis* to *trans* isomerization requires less motion than has previously been assumed.<sup>6-8</sup> Similar suggestions have been made recently by others.<sup>59</sup> In particular, paddle wheel like motion of the benzene rings may not be required, and instead, *cis* to *trans* isomerization might occur via substantial movement of the ethylenic hydrogens and carbons combined with slicing motion of the benzene rings. This isomerization pathway is consistent with the weak correlation observed between friction and viscosity (reflected in the weak viscosity dependence observed when changing solvent). A weak viscosity dependence of the isomerization rate has also been reported for 2-vinylnanthracene,<sup>60</sup> which has a relatively small isomerizing group. Involvement of ethylenic carbon and hydrogen motion in the *cis* to *trans* isomerization of stilbene may also explain the 10%–24% increase in lifetime upon deuteration of the ethylenic hydrogens. If the *cis* to *trans* isomerization involves a substantial amount of ethylenic hydrogen motion, as has been suggested,<sup>33,34</sup> then isotopic substitution would probably reduce the rate. Unfortunately, the large uncertainties in our isotope results, especially for tetradecane, make it difficult to determine if the deuterium isotope effect arises from a change in the *cis* to *trans* or the *cis* to DHP isomerization rate.

## C. Temperature dependence and activation energy

Using the ideas about friction and the excited state potential energy surface just discussed, we can more critically evaluate and interpret our studies of the temperature dependence of the decay time, learn more about the barrier for the *cis* to *trans* isomerization, and better understand the solvent influence on the potential energy surface.

The curvature observed in the *cis*-stilbene isoviscosity Arrhenius plots in short alcohol solvents [see Fig. 4(b)] may result from either a changing relationship between friction and viscosity or a change in the potential energy surface due to rapid solvation, most likely for the *cis* to *trans* reaction. As the chain length is increased, the activation energy for the *cis* to *trans* isomerization may increase as a result of a decrease in solvent polarity and solvation rate [due to differential solvation of  $S_2$  (Refs. 17, 18)]. At *n*-pentanol there is a substantial drop off of the rate in the 2.36 cp isoviscosity plot, consistent with our suggestion that at this chain length *cis*-stilbene effectively sees an alkane environment in *n*-alcohols. It is also likely that  $\eta/\zeta$  changes between the various alcohol solvents in a

more complex manner than in the alkanes. A plot of rotational reorientation time for *trans*-stilbene in *n*-alcohols vs  $\eta/T$  at 298 K (Ref. 52) is clearly non-linear and has a point of inflection, supporting this conjecture.

The presence of two reaction channels also complicates the interpretation of the isoviscosity Arrhenius plot in alkanes. In order to isolate the contribution of the *cis* to *trans* barrier to the total activation energy we will use various estimates of the *cis* to DHP reaction rate and its temperature dependence to adjust our data. For the sake of subtracting out the DHP contribution, we shall assume that the excited *cis*-stilbene to DHP rate follows an Arrhenius law of the form,

$$k_{\text{DHP}} = \nu_a \exp(-E_{\text{DHP}}/k_b T) \quad (6)$$

with an activation energy of  $E_{\text{DHP}}$ . An activation energy of 8.5 kJ/mol ( $710 \text{ cm}^{-1}$ ) was obtained recently for *cis*-stilbene in hexane by Nikowa *et al.*<sup>8</sup> An earlier experimental activation energy of 1.2 kcal/mol ( $420 \text{ cm}^{-1}$ ) was reported for *cis*-stilbene in a 2 to 1 mixture of methylcyclohexane and 2-methyl pentane.<sup>10</sup> These can be compared to a recent theoretical estimate of  $535 \text{ cm}^{-1}$ .<sup>36</sup> For the earlier experimental activation energy of  $420 \text{ cm}^{-1}$ , there was no determination of the absolute value of the rate at a given temperature and therefore no way to estimate the frequency factor,  $\nu_a$ . With the recent activation energy of  $710 \text{ cm}^{-1}$ , determined in hexane, we can use Nikowa *et al.*'s<sup>8</sup> room temperature extrapolation to  $k_{\text{DHP}}$  to determine  $\nu_a$ . The value of  $k_{\text{DHP}}$ , however, is significantly different in other alkane solvents at this temperature. Using the uncertainties given by Nikowa *et al.*<sup>8</sup> for the *cis*-stilbene excited state lifetimes, we estimate that the inferred values of  $k_{\text{DHP}}$  in *n*-hexane ( $2.0 \times 10^{11}$ ) and *n*-nonane ( $3.3 \times 10^{11}$ )<sup>8</sup> differ from each other by 3 to 5 standard deviations. If their extrapolation is correct, then this variation presents a problem—our calculation would require the room temperature rate, and possibly the activation energy for each solvent used in the isoviscosity Arrhenius plot.

We wish to obtain a rough estimate of the magnitude of the correction for DHP formation and its general effect. We therefore assume that the rate of DHP formation is constant in the alkanes, has a rate from  $2.0\text{--}2.7 \times 10^{11} \text{ s}^{-1}$  at 295 K, and a barrier between 420 and  $710 \text{ cm}^{-1}$ . Using these calculated DHP formation rates to correct our isoviscosity activation energy, we obtain activation energies for the *cis* to *trans* isomerization between 190 and  $370 \text{ cm}^{-1}$ . Since we have not corrected for the expected decrease in the ratio of friction to viscosity as chain length is increased, these values are probably still upper limits to the *cis* to *trans* barrier.

In order to estimate the activation energy for the *cis* to *trans* isomerization process under true isofriction conditions, we assume the slopes,  $A$ , from the pressure dependence studies of Nikowa *et al.*<sup>8</sup> are proportional to the ratio of viscosity to friction in solvents. We will use the lifetime obtained in octane at 266 K and 0.78 cP. From the slopes in octane and hexane,<sup>8</sup> we calculate that  $0.55 \pm .03$  cp in hexane would yield the same friction as 0.78 cp in

octane. We then determine the hexane lifetime at 0.55 cp using the fit to Eq. (2) for *n*-hexane.<sup>8</sup> From the 0.55 cp hexane and 0.78 cp octane decay rates we obtain an isofriction Arrhenius activation energy of  $-40 \pm 136 \text{ cm}^{-1}$ . The large uncertainty results from using two data points separated by only 27 °C. Correcting the two isofriction decay rates using a conservative estimate of the rate of DHP formation in these solvents with rate,

$$1.551 \times 10^{12} \exp(-420 \text{ cm}^{-1}/kT)$$

we obtain an activation energy for the *cis* to *trans* process of  $-298 \pm 136 \text{ cm}^{-1}$ . Although our isoviscosity Arrhenius plot yields an upper limit to the *cis* to *trans* barrier of  $386 \text{ cm}^{-1}$  in alkanes, values within a few hundred  $\text{cm}^{-1}$  of zero (plus or minus), are consistent with our data.

## V. CONCLUDING REMARKS

Our results suggest that the potential energy surface for both the *cis* to *trans* and *cis* to DHP excited state isomerization reactions is not significantly altered between polar and nonpolar solvents for longer *n*-alcohols and *n*-alkanes. Apparently, the friction experienced by *cis*-stilbene during *cis* to *trans* isomerization is mostly determined by the local solvent environment. We suggest that the proportionality between friction and viscosity may remain approximately constant in a single solvent as pressure (and temperature) is changed but changes from one solvent to another. We place an upper limit on the *cis* to *trans* barrier of  $386 \pm 29 \text{ cm}^{-1}$  in nonpolar liquids, consistent with the activation energy determined by Saltiel *et al.*,<sup>32</sup> estimated by Nikowa *et al.*,<sup>8</sup> and the long lived fluorescence observed for *cis*-stilbene in noble gas clusters.<sup>30</sup> Correcting for the temperature dependence of DHP formation yields a range of *cis* to *trans* activation energies centered around zero.

For testing the ideas and interpretations we propose, it would be very useful to obtain accurate product quantum yields in alkane and alcohol solvents, especially those of the same chain length (e.g., decane and decanol). It would also be valuable to study rotational reorientation times vs  $\eta/T$  in a single solvent for the *n*-alcohols (and cyclohexane), to see if they are linear and search for trends in the slopes. In particular, differences in the proportionality between friction and viscosity resulting from changes in solvent size and hydrogen bonding effects may yield slopes that do not vary in a simple fashion.

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