TABLE II: Ratio of Partial Pressures of C70 over C60

	$[P(C_{70})/P(C_{60})] \times 100^{a}$		
run	T = 667 K	T = 800 K	
1	3.7	8.1	
2	5.6	9.2	
3	5.3	9.5	
4	5.0	5.6	
5	4.3	5.9	
6	4.2	5.5	
ref 3	12.8 (613 K)		

^aCorrected for ionization cross sections:

$P(C_{70})/P(C_{60}) = 60I(C_{70}^{++})/70I(C_{60}^{++})$

 $(C_{24}H_{12})$ and ovalene $(C_{32}H_{14})$, have been included. The temperature, T, represents the mean temperature of each run. The lower value for the heat of sublimation of C_{60} reported in the previous publication should be considered as that of an amorphous C_{60} , where the sample was undergoing a change during the experiment.⁸ The more scattered values of the heats of sublimation of C_{70} may have resulted from the low intensities of the C_{70}^{++} ion. However, it is clear that in a polycrystalline C_{60} matrix, C_{70} has a slightly higher heat of sublimation than C_{60} .

Table II lists the ratio of C_{70} to C_{60} calculated at two temperatures by using the second-law plots for each of the six runs.

The ion intensities read from the plots were converted to relative partial pressures by assuming that the ionization cross sections were directly proportional to the number of carbon atoms in the ions. Thus

$$\frac{P(C_{70})}{P(C_{60})} = \frac{60I(C_{70}^{++})}{70I(C_{60}^{++})}$$

As expected from the difference in heats of vaporization, the amount of C_{70} in the vapor phase relative to C_{60} increased with increasing temperature.

The heats of vaporization measured for C_{70} for runs 4–6 differ slightly from those measured for the first three runs, but the C_{60} heats of vaporization do not show this anomaly. In addition, the calculated C_{70} : C_{60} ratio for runs 1–3 differs from that determined for runs 4–6. We do not know the reason for these observations, although we note that the sample was allowed to sit at room temperature in air for 2 weeks between runs 3 and 4. Selective oxidation of C_{70} , leading to lesser amounts of this species, could account for the observed difference in the C_{70} : C_{60} . The data may also suggest that at higher concentrations of C_{70} the increased probability of interactions between adjacent C_{70} molecules in a C_{60} matrix leads to a higher heat of vaporization for C_{70} .

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Femtosecond Laser Study of the Alignment of Reactant and Products in the Photolsomerization Reactions of *cis*-Stilbene

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Polarized femtosecond laser studies of the products of the photoisomerization of *cis*-stilbene demonstrate an unexpectedly high degree of alignment between the cis reactant and trans product transition dipoles and an unexpectedly low degree of alignment between the cis reactant and dihydrophenanthrene (DHP) product transition dipoles. These results are consistent with the reaction toward both trans and DHP involving a significant angular displacement of the ethylene bond. Some possible reasons for this displacement are discussed.

Time-resolved spectroscopic studies of the photoisomerization of *cis*-stilbene have yielded a great deal of information on this simple reaction.¹⁻⁶ The isomerization of electronically excited *cis*-stilbene (cis^{*}) occurs in 1–2 ps even in high-friction environments.^{5,6} As this is much faster than the rotational diffusion, the intramolecular rearrangement occurs while the molecule is essentially fixed in space. In this situation the alignment of the reactant and product molecules can be measured with polarized light pulses and hence the reaction coordinate can be determined. We have performed such a study of the photoisomerization of *cis*-stilbene. The femtosecond transient absorption spectrometer used for these experiments has been described previously.⁵ The pump wavelength was 312 nm. A flowing sample of *cis*-stilbene (less than 0.1% *trans*-stilbene) in hexadecane was used for all measurements. *cis*-Stilbene excited at 312 nm forms *trans*-stilbene and dihydrophenanthrene (DHP) with quantum yields of 0.35 and 0.10, respectively.⁷ The remaining cis* molecules return to the ground electronic state on the same time scale as DHP and trans formation.

The time-resolved absorption of *cis*-stilbene probed between 540 and 420 nm exhibits a transient which decays in 1.4 ps due to the excited state of *cis*-stilbene, and a persistent increase which rises in ≤ 1.7 ps. The time-resolved absorption obtained by using a 480-nm probe is shown in Figure 1. The persistent spectrum found between 540 and 420 nm is consistent with the known spectrum of ground electronic state DHP ($\lambda_{max} = 450 \text{ nm}^8$). A persistent absorption signal is also observed by using probe

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Figure 1. Time-resolved absorption signal obtained when a sample of cis-stilbene is pumped at 312 nm and probed at 480 nm. The inital transient decays in 1.4 ps, consistent with the decay of cis* obtained throughout the visible and UV region of the spectrum,⁵ to a persistent absorption assigned to DHP. The inset contains more precise absorption and anisotropy data obtained at early times. The error bars represent the 90% confidence level from a statistical analysis of the data. The solid line drawn through the anisotropy data represents a fit to the data assuming different initial values of the anisotropy for the cis* and DHP absorptions and the same overall reorientation time of 60 ps.

wavelengths between 345 and 312 nm⁵ due to ground-state trans and DHP product absorptions which dominate the bleaching of the cis absorption.

The anisotropy of the photoproduct absorption is defined as $r(t) = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$, where I_{\parallel} and I_{\perp} are the absorption signals for probe polarizations parallel and perpendicular to the pump polarization. From the data for cis \rightarrow DHP probed between 540 and 420 nm we obtain a value of $r_{CD}(0) = 0.17 \pm 0.03$ (see inset in Figure 1). The cis \rightarrow trans anisotropy ($r_{\rm CT}$) probed in the ultraviolet region may be determined by using the known quantum yields of the photoproducts and the steady-state relative extinction coefficients.⁸ This analysis brackets the possible values for the cis \rightarrow trans anisotropy $0.15 \le r_{\rm CT}(0) \le 0.26$. The best value of $r_{\rm CT}(0)$ as derived from these absorption measurements is $0.18 \pm 0.03.9$

In another experiment, ground-state trans was generated from cis with a 312-nm pump and its fluorescence induced by a delayed 312-nm probe. The integrated fluorescence signal from appropriately polarized pump and probe beams provides the transstilbene anisotropy independently of the presence of cis and DHP.10 Typical data is shown in Figure 2. In this measurement the anisotropy of the trans signal was determined to be $r_{CT}(0) = 0.22$ ± 0.03.

Because of the assumptions used to separate the trans and DHP contributions to the ultraviolet absorption signal, and the fact that the extraction of the anisotropy from the fluorescence experiment is slightly model dependent (see ref 10), we have taken the average of the two measurements as the best value for $r_{CT}(0)$. Thus, we obtain a value of $r_{\rm CT}(0) = 0.20 \pm 0.04$.

The product anisotropy at the earliest time, $r_{CP}(0)$, measures $0.4\langle P_2[\cos\theta_{CP}(0)]\rangle$, where $P_2[x]$ is the second Legendre polynomial, θ_{CP} determines the alignment of the cis and trans (θ_{CT}) or cis and DHP (θ_{CD}) transition dipoles, and $\langle \rangle$ is an average over a frame fixed in the cis molecule. Accurate measurements of the average alignments of the trans and DHP transition dipoles relative to the cis-stilbene precursor place constraints on the nature of the



Delay Time (ps)

Figure 2. Trans fluorescence rise curves obtained from a sample of cis-stilbene pumped at 312 nm and probed at 312 nm. The fluorescence is detected by a photomultiplier tube through a 12-nm band-pass interference filter centered at 350 nm as discussed in ref 10. Negative times in this figure indicate only the change in designation of the two 312-nm pulses as pump and probe. The solid curves are referred to the upper time scale while the dashed curves are referred to the lower time scale. The designations ZZ, ZX, and XZ indicate the relative polarizations of the pump and probe beams. The perpendicular curve (ZX, XZ) is not symmetric because the total fluorescence signal propagating along Z is dependent on the polarization of the probe pulse (which excites the fluorescence) even for infinite delay times between the pump and probe pulses.

reaction coordinate and help to identify the motions involved in the isomerization.

The trans transition dipole $(S_0 \rightarrow S_1)$ is directed along the longest in-plane axis of the molecule.¹¹ A calculation by Dick¹² has predicted the cis $(S_0 \rightarrow S_1)$ transition dipole to lie very close to the ethylene bond as expected from simple π -electron considerations. A simple exciton model also predicts the DHP ($S_0 \rightarrow$ S_1) transition dipole to be directed along the longest polyene axis, perpendicular to the C_2 symmetry axis.¹³ From symmetry considerations it is unlikely that the actual transition dipoles will deviate much from these predicted directions.

The values of $\langle \cos^2 \theta_{\rm CT} \rangle^{1/2} = 0.82 \pm 0.04$ and $\langle \cos^2 \theta_{\rm CD} \rangle^{1/2}$ = 0.79 ± 0.03 obtained from these measurements are most simply interpreted by assuming a narrow distribution of alignments in which case $\theta_{CT} = 35 \pm 4^{\circ}$ and $\theta_{CD} = 38 \pm 3^{\circ}$. This value of θ_{CT} is significantly *smaller* and that of θ_{CD} is significantly *larger* than expected for the most obvious reaction coordinates. The simple rotation about the ethylene bond along the traditional reaction coordinate⁵ predicts $\theta_{CT} = 60^{\circ}$, while a ring closure to DHP by phenyl ring rotation yields $\theta_{CD} \approx 7^{\circ}$. Our results therefore indicate that the reaction toward both trans and DHP is accompanied by a significant angular displacement of the ethylene bond.

One depiction of the required motion of the ethylene carbons which preserves the direction of the C_2 axis in space and which involves no overall motion in the laboratory frame either as a result of rotational diffusion or as a result of torques from the interdependence of internal and external motions is shown in Figure 3. An appropriate reorientation of the ethylene bond will occur during the reaction when a rotary motion of the ethylene carbons is the initial motion. Such a motion is consistent with the expectation that ethylenic carbons will have a tendency toward sp³ hybridization in the S₁ state.¹⁴ Pyramidalization may be achieved largely by a motion of these carbon atoms (by a few tenths of 1 A) and the ethylenic hydrogen atoms. This motion would be followed by slower ethylene bond torsions and phenyl ring rotations to form equilibrated trans-stilbene or DHP. The motion of the

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Figure 3. A proposed initial reorientation of the ethylene bond accounting for the measured anisotropy: The common C_2 symmetry axis is fixed. The vectors shown are perpendicular to C_2 . A conventional rotation about the ethylene bond $(\hat{E}(0))$ after pumping the cis transition dipole, \hat{C} , leads to trans, \hat{T}_0 . A rotation of the ethylene bond to $\hat{E}(t)$ is required to fit the measured $\langle \cos^2 \theta_{CT} \rangle^{1/2}$.

ethylene bond suggested by the present measurements is consistent with the initial geometry change deduced from a resonance Raman study of *cis*-stilbene.¹⁵ Petek et al.¹⁶ recently proposed a different reaction coordinate but made no explicit mention of an ethylene bond rotation.

A full interpretation of the anisotropy results reported in this paper must include consideration of whether the isomerizing molecules might rotate in the laboratory frame about a definite axis fixed in each molecule. In order to minimize the friction on the cis to trans isomerization, the whole molecule may be forced to rotate in order to minimize the volume swept out in the process. Furthermore, the conrotatory motions of the phenyl rings of a cis-like structure must generate a torque that could lead to a significant reorientation of the whole molecule. Such effects involving the coupling of internal and overall motions have been considered by Moro for butane isomerization.¹⁷

In general, the forces generating a reorientation in the laboratory frame would be expected to be different for the cis to DHP reaction and the cis to trans reaction. The traditional reaction pathway for cis to DHP involves primarily a phenyl ring rotation. In this pathway, the overall motion required to minimize the volume swept out in the isomerization process is small since the principal diffusion axes of reactant and product thus formed are nearly parallel. However, our anisotropy results discussed above are indicative of a significant angular displacement of the ethylene bond in both the cis to trans and cis to DHP reactions. These results suggest that if the reorientation of the isomerizing molecule is dominated by the coupling of internal and overall motions it is most likely to occur as a result of phenyl ring rotations common to both the DHP and trans reaction coordinates. Phenyl ring rotation is necessarily included in both of the reaction coordinates discussed in the literature.15,16

Clearly additional experimental and theoretical efforts are needed to separate the various angular motions discussed above. Both a modified reaction coordinate involving the pyramidalization of the ethylenic carbon atoms and the coupling of internal and external motions, in particular the effect of the phenyl ring rotations, must be considered in a full interpretation of the results. Such a study is underway.

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