Photoisomerization Dynamics of Stiff-Stilbene in Solution

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Supporting Information

ABSTRACT: Photoinduced isomerization of 1,1′-bis-indanylidene (stiff-stilbene) in solution was studied with broadband transient absorption and femtosecond Raman spectroscopies, and by quantum-chemical calculations. Trans-to-cis S1 isomerization proceeds over a 600 and 400 cm−1 barrier in n-hexane and acetonitrile, respectively. The reaction develops on multiple time scales with fast (0.3–0.4 ps) viscosity-independent and slower (2–26 ps) viscosity-dependent components. In the course of intramolecular torsion (which should be the main reaction coordinate) some excited molecules pass through the perpendicular conformation P and reach the cis geometry, to be temporarily trapped there. Subsequently they relax back to P and further to the ground state S0. The cis-to-trans isomerization reveals ultrafast (0.06 ps) oscillatory relaxation followed by 13 ps decay in n-hexane and 2 ps decay in acetonitrile, corresponding to barriers of 800 and 400 cm−1, respectively. Raman S0 and S1 spectra are reported and discussed. The perpendicular conformation P was not detected, possibly due to its low oscillator strength and short lifetime, or because of strong overlap with hot product spectra. XMCQDPT2 calculations locate a stationary point on the cis side and two perpendicular-pyramidalized stationary points, to be reached from the former over 300 and 680 cm−1 barrier. Implications for parent stilbene are discussed; in this case we also see evidence for the trans-to-cis adiabatic path, as in stiff-stilbene. Very similar viscosity dependence for the two compounds supports the common isomerization pathway: torsion about the central double bond.

1. INTRODUCTION

Photoisomerization of trans-1,1′-bis-indanylidene (stiff-stilbene, or briefly stiff) has initially been studied1−4 in connection with stilbene photochemistry.5−22 Phenyl twisting is hindered in stiff and this restriction may simplify the main isomerization path, torsion around the central double bond, and its manifestation in time-resolved spectra. Therefore stiff is an important model for studying the photoisomerization process. Other promising applications of this compound are related to molecular force probing23 and the development of light-driven nanomotors24,25 in which stiff serves as the key unit.

Absorption spectra of trans-stiff in solution are shown in Figure 1. They are similar to those of parent stilbene but slightly red-shifted and reveal better-resolved vibrational structure since phenyl twisting is hindered.3 First transient absorption measurements were performed in 1983 by Hochstrasser and co-workers.1,2 They found that the reaction is strongly viscosity-dependent, having 3 ps reaction time in hexane and 26 ps in hexadecane.1,2 This is much faster compared to trans-stilbene, which isomerizes in the same solvents with 84 and 163 ps, respectively.9−14 The rapid isomerization was exploited in a search for an intermediate of perpendicular molecular geometry P. The authors found an indication of P and estimated its lifetime to be 10 ps.2 Later Fuss et al.7 investigated trans-stiff in a supersonic jet and reported the formation of P and its decay with 0.18 and 0.8 ps, respectively. The pronounced viscosity dependence has been widely used to test Kramers’ theory of chemical reactions.1,11 Satisfactory agreement between Kramers’ model and experiment was reported for stiff-stilbene1 and parent stilbene11−13 and for 1,4-diphenylbutadiene.11,26,27

Important computational work was performed by Improta and Santoro.8 Their time-dependent density functional theory (TDDFT) study of the vertical transitions in trans (t-stiff) and cis (c-stiff) isomers suggests that the S1 state is dominated by the HOMO–LUMO excitation and is well separated energetically from higher states. Unlike unsubstituted stilbene, t-stiff was found to have barrierless torsion in S0, while for c-stiff a true unconstrained stationary point was located with a minor barrier of 50−100 cm−1 toward perpendicular geometries. Unfortunately, conventional TDDFT cannot correctly treat this perpendicular domain where strong interaction with doubly excited electronic configurations takes place. A recent spin-flip TDDFT study,19 of parent stilbene is pointed out here as an example of efficient improvement at low computational cost.

Very recently, Liu and Morokuma20 performed a CASPT2/CASSCF(10,10) study of polymethylated stiff-stilbene applied as a molecular rotor. The authors calculated also stiff and parent
stillbene in the full range of torsion, though only under the C₆ symmetric constraints and at the CASSCF(10,10) level which does not take into account the dynamic correlation effect.

In the present paper we report new experimental and computational results on the excited-state evolution of stilbene. Compared to earlier experiments, our broadband transient absorption spectroscopy provides higher temporal resolution and allows for a complete record of spectral evolution including bleach, stimulated emission and excited-state absorption. We investigate both the trans-to-cis and cis-to-trans isomerization path following optical excitation into the full range of torsion, though only under the symmetric constraints and at the CASSCF(10,10) level which does not take into account the dynamic correlation effect.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1. Compounds and Isomerization Yields. trans-1-(1-Indanylidene)jindane (t-stiff) was prepared according to ref 4. To a suspension of titanium tetrachloride (0.91 mL, 8.3 mmol, 1.1 equiv) and zinc powder (1.09 g, 16.6 mmol, 2.2 equiv) in anhydrous tetrahydrofurane (80 mL) under argon at 0 °C, 1-indanedione (1.00 g, 7.6 mmol, 1.0 equiv) was added slowly. The resulting reaction mixture was stirred at 65 °C for 8 h. The mixture was allowed to cool to room temperature before it was poured into a saturated solution of sodium carbonate (200 mL). The aqueous phase was extracted with diethylether (50 mL) and three times with petroleum ether (75 mL). The combined organic phases were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica eluting with petroleum ether and in the absence of light. Pure t-stiff was isolated as colorless crystals (0.53 g, 2.27 mmol, 60% yield). Melting point and NMR-spectra are in agreement with the literature. Solvents from Merck (Uvasol) were used as delivered, and aliphatic solvents were all normal (n-hexane etc).

c-Stiff was prepared photochemically as illustrated by Figure 1. A 50 mL hexane solution of t-stiff at 1g/L concentration was illuminated with 313 nm light. Argon bubbling was applied to prevent 2,2′ cyclization. A photostationary spectrum (green) corresponds to 63% of cis and 37% of trans isomer. This solution was used for cis transient measurements.

The cis-to-trans and trans-to-cis isomerization yields, Ytc = Yct = 0.36 ± 0.01 in hexane and 0.31 ± 0.01 in acetonitrile, were determined by the actinometry method under illumination at 339 nm (Figure 1). The measurement protocol is described in the Supporting Information (SI). From transient measurements the yields are determined to be the same in both solvents; therefore we use Ytc = Yct = 0.33 in the following.

2.2. Transient Absorption (TA). The setup has been described in detail elsewhere. A Ti:Sapphire amplifier delivers 30 fs, 500 μJ, 500 Hz pulses at 800 nm. The beam is split in two with 380 and 70 μJ. The 380 μJ are used to pump an optical parametric amplifier which provides 50 fs, 2 μJ pulses in the range 300–350 nm. The 70 μJ are converted into 400 nm, 12 μJ pulses to generate a probe supercontinuum in a 1 mm CaF₂ plate. The probe light is spectrally filtered and then split for signal and reference. The signal beam is imaged onto the sample flow cell at a spot size of 100 μm. The sample (t-stiff or c-stiff in solution) is 0.2–0.3 nm thick and has absorbance A ≈ 0.7 at the peak. Signal and reference pulses are dispersed separately with gratings polychromators and registered by photodiode arrays (512 pixels) covering the range 275–690 nm.

TA spectra ΔA(λ, t) were measured at 20.5 °C with parallel, perpendicular and magic angle polarization. Pump–probe scans were recorded from negative-to-positive and back from positive-to-negative delays in order to reduce low-frequency noise, with 0.02, 0.2, and 0.4 ps steps, averaged over multiple (16–24) scans and time-corrected for the chirp of the probe. The instrument response was below 0.1 ps (fwhm) over the entire spectral range. Transient anisotropy spectra ρ(λ, t) = (ΔA|| − ΔA⊥)/(ΔA|| + 2ΔA⊥) are calculated, and rotational diffusion times, τD, are obtained from monoexponential decays of ρ(λ, t) averaged over the relevant spectral range.

For t-stiff the excitation wavelength Δλexc = 340 nm is chosen close to the 0–0 transition; c-stiff is excited with 350 nm where trans absorption is weak. A residual trans contribution was eliminated from cis spectra by subtracting t-stiff spectra which were recorded separately with the same 350 nm excitation.

2.3. Femtosecond Stimulated Raman (FSR). The FSR setup is similar to the TA setup, only a picosecond Raman excitation is added and the polychromator dispersion is set to 2 cm⁻¹/pixel to cover a 1000 cm⁻¹ probe range. The pump–probe cross-correlation is 0.08 ps (fwhm), the spectral resolution is 10 cm⁻¹, and the positions of Raman bands are determined with ±2 cm⁻¹ accuracy. For t-stiff the UV pump...
and Raman excitation wavelengths are 340 and 619 nm, while for c-stiff they are at 351 and 692 nm, respectively.

2.4. Computational. To optimize the geometry of stiff-stilbene in the $S_0$ and $S_1$ states we used the extended multiconfigurational quasi-degenerate second order perturbation (XMCQDPT2) theory,\(^{33}\) which is implemented in the Firefly quantum chemistry package\(^{34}\) partly based on the GAMESS(US)\(^{35}\) source code. Similar to parent stilbene,\(^{28}\) a correct description of $S_1$ requires the consideration of six CASSCF roots in case of a symmetry-less calculation. We therefore employed the XMCQDPT2/SA6-CASSCF(10,10)/cc-pVDZ scheme (hereinafter SA6-XMCQDPT2(10,10)) with equal-weight averaging over the six lowest roots. In this way comparable quality is obtained in describing $S_0$ and $S_1$ in both symmetric and asymmetric configurations. We selected the (10,10) π-orbital active space that omits the two lowest occupied (nodeless) and the two highest unoccupied (6-node) benzenoid orbitals. This compromise allows a direct numerical XMCQDPT2 optimization without sacrificing accuracy in describing the lowest excited states, where excitations involving the omitted orbitals are of minor importance. Calculations were performed with 12 states in the model space, frozen chemical core, and an intruder-state avoidance (ISA) shift of 0.02 hartree.

3. EXPERIMENTAL RESULTS

3.1. t-Stiff TA Spectra and Kinetics. Transient absorption spectra $\Delta A(\lambda, t)$ of t-stiff in n-hexane upon 340 nm excitation are shown in Figure 2. Bleach and stimulated emission (SE) are negative while excited-state absorption (ESA) is positive, having a strong absorption peak at 540 nm. At early delays ($-0.06 < t < 0.06$ ps, top left) the signal rises in intensity with no spectral shifts. Sharp vibronic features around $t = 0$, when pump and probe pulses overlap in time, are due to coherent contributions to the signal. Spectral bands can be assigned to the excited t-species and are labeled tSE and tESA. Note that the early tESA extends to the red edge of our observation window, in what looks like a shoulder or pedestal to the dominant band. The early tSE band reproduces very well the stationary emission in glycerol (Figure S1 in the SI), in which case torsional motion, and therefore internal conversion, should be impeded. From the identity of the two emission spectra it follows that ultrafast vibrational relaxation, including some relaxation along the reaction coordinate, is either absent or not resolved. Substantial evolution is observed starting from $t = 0.06$ ps (bottom left). The tSE band, initially peaked near 350 nm, appears to decay with $r_1 = 0.3$ ps as it shifts by 50 nm to the red. Simultaneously the strong tESA peak decays with 0.4 ps and shifts from 545 to 555 nm, whereas on the red shoulder a weak absorption band at 650 nm rises on the same time scale. We shall see later that this new band is characteristic for the cis-species; therefore (and without loss of generality) it is labeled cESA in the figure. Its rise with 0.4 ps time constant suggests that excited molecules may pass, in the course of torsion, through the perpendicular conformation $P$ and reach the cis geometry. While the aforementioned changes take place, the bleach spectrum below 330 nm does not change, from which we conclude that the evolution before $t = 1$ ps occurs mainly in the excited state. That is, most of the molecules which reach $P$ on this time scale do not relax to the ground state but continue their torsion toward the cis conformation.
At longer delays ($t > 1$ ps, top right) the excited-state absorption for $\lambda > 480$ nm decays with $\sim 5$ ps, but the evolution at the 650 nm band is slower compared to the evolution at the peak. If the aforementioned interpretation is correct, then the difference implies a higher cis isomerization barrier compared to the trans one. Bleach recovery takes place also with 5 ps, indicating that the perpendicular intermediate is short-lived. A $P$ band, expected between 320 and 380 nm as in cis-stilbene$^{18}$ and 1,1'-dimethylstilbene,$^{22}$ is not observed however. A reason for this may be that emission and hot absorption of t- and c-products lie in same spectral range, making differentiation impossible. The observation of DHP proves the existence of the intermediate c-species in the excited state, as it is necessary for DHP production.

In the bleach region the signal at $t = 100$ ps can be evaluated as follows. Just after excitation the bleach spectrum $\Delta A(\lambda,0) = -n_0 A_c(\lambda)$ is proportional to excited population $n_0$ and trans absorption $A_t(\lambda)$. The bleach recovers at late time as the excited species return to the electronic ground state and cool down. Assuming yield $\alpha$ for the ground-state cis isomer, $\beta$ for DHP, and $(1-\alpha-\beta)$ for the trans isomer one has

$$\Delta A(\lambda, \infty) = n_0 [\alpha(A_c - A_t) - \beta A_t + \beta A_{DHP}]$$

$$\Delta A(\lambda, 0) = \alpha(1 - A_c/A_t) + \beta A_{DHP}/A_t$$

where $A_c(\lambda)$ is the cis absorption. In particular, when $\beta = 0$, late bleach spectra $\Delta A(\lambda, \infty)$ are proportional to the difference absorption $(A_c - A_t)$. Generally $\beta \neq 0$, and its value affects the spectral shape of the signal. This can be used to estimate the DHP yield, by fitting the bleach spectra with eq 1. In Figure 2 (bottom right) the fit corresponds to $\beta = 0.03$, $\alpha = 0.33$.

Growth and decay of spectral bands are analyzed with the help of band integrals

$$I(\lambda_1, \lambda_2, t) = \int_{\lambda_1}^{\lambda_2} \Delta A(\lambda, t) \, d\lambda/\lambda$$

With a careful choice for the range $(\lambda_1, \lambda_2)$ a band integral can be made roughly proportional to a corresponding time-dependent population. Decays of band integrals are fitted triexponentially, $a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) + a_3 \exp(-t/\tau_3)$. Figures 3 and 4 show the short and long-time behavior, respectively, of SE, ESA, and bleach. The fast time $\tau_1$ (0.3 ps for tSE and 0.4 ps for tESA peak) is viscosity-independent, although its amplitude decreases with higher viscosities. The slow components $\tau_2$ and $\tau_3$ are strongly viscosity-dependent. Fit parameters are summarized in Table 1, together with rotational diffusion or anisotropy decay times $\tau_R$ and solvent viscosity $\eta$.

For easier comparison we also give an average slow time, $\tau_{av} = (a_2 \tau_2 + a_3 \tau_3)/(a_2 + a_3)$. Note that tSE decays approximately twice as fast as ESA, even though the two bands are associated with the same excited-state population.

Lastly for trans, Figure 5 shows the microviscosity dependence of bleach recovery (or isomerization) time $\tau_R$. The microviscosity is expressed by the anisotropy decay (rotational diffusion) time $\tau_R$ measured in the same bleach region. For comparison the dependence for trans-stilbene is also shown, in which case the isomerization time $\tau_{av}$ was divided by 7 to have the two graphs in the same numerical range.

### 3.2. c-Stiff TA Spectra and Kinetics

Transient spectra of c-stiff in acetonitrile are displayed in Figure 6, where the top right panel shows the evolution on the picosecond time scale. At 0.5 ps, for example, the SE band (peaked at 440 nm) agrees with the one obtained from stationary cis fluorescence, and an ESA band at 650 nm resembles strongly the one found with the cis-stilbene parent$^{18}$ therefore cSE and cESA can be assigned with confidence. Also a weak band X is seen on the blue flank of cESA. Afterward the cSE and cESA bands decay with 2 ps in acetonitrile and 13 ps in hexane (Figure S4). At 100 ps (bottom right) the absorbance by the DHP product is related to changes in the bleach region, similar to the case of t-stiff but with bleach signals inverted.

Tracing backward to earlier delays (at left) we see that X is dominant before 0.12 ps; in fact it appears to be the precursor of cESA in a process of spectral change, which has about 0.06 ps time constant.

Figure 7 compares transient cis and trans spectra in hexane. Spectra have been normalized to equal excited populations and thus reflect the relative strength of bands. Early cis and trans ESA bands (for example at 0.1 ps) have comparable strength, unlike in parent stilbene where the trans ESA bands are much weaker.
stronger than their cis analogues.\textsuperscript{18} Here the effect is evidently due to the stiffness of the studied molecule.

Short-time kinetics from t- and c-stiff in hexane are compared in Figure 8 for three characteristic wavelengths. The 555 nm kinetics clearly shows different response of the trans and cis isomers. An ultrafast (0.06 ps) oscillatory component is prominent for the c-species but absent for the t-species. Therefore the 550 nm band X in Figure 6, even though it is similar in shape and position to tESA (Figure 2), cannot originate from trans impurities but must be ascribed to the c-species that was excited originally. In this connection remember also that all transient absorption data of c-stiff, as shown in the figures and tables, have previously been corrected for a small t-stiff contribution, which was measured separately.

The long-time kinetics of c-stiff in hexane is shown in Figure 9. A biexponential fit of the cESA decay gives \( \tau_2 = 4.9 \) ps, \( a_2 = 0.15 \), \( \tau_3 = 13.9 \) ps. An ultrafast component \( \tau_1 = 0.06 \) ps may possibly be related to intermediate t-species created in the course of the cis-to-trans isomerization, similar to the intermediate c-species observed in the trans-to-cis isomerization.

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Table 1. Excited-State Decay Parameters Following Excitation of trans- and cis-Stiff in Solution

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity ($\eta$, in cP)</th>
<th>Anisotropy ($\tau_R$, in ps)</th>
<th>$\tau_{350\text{ nm} , \text{tSE}}$</th>
<th>$\tau_{550\text{ nm} , \text{tESA}}$</th>
<th>$\tau_{420\text{ nm} , \text{cSE}}$</th>
<th>$\tau_{650\text{ nm} , \text{tESA} + \text{cESA}}$</th>
<th>Bleach $\tau_2$, $\tau_3$, $\tau_\text{av}$</th>
<th>Barrier ($\text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>0.86</td>
<td>1.5</td>
<td>2.1</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
<td>10.4</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.31</td>
<td>3.8, 14(11%), 4.9</td>
<td>3.9</td>
<td>4.9, 14(16%), 6.4</td>
<td>2.9, 16(25%), 6.2</td>
<td>10.4</td>
<td>2.3</td>
<td>10.4</td>
</tr>
<tr>
<td>Octane</td>
<td>0.55</td>
<td>6.1, 20(11%), 7.6</td>
<td>6.4</td>
<td>7.5, 18(13%), 8.9</td>
<td>5.7, 23(27%), 8.9</td>
<td>2.3</td>
<td>10.4</td>
<td>2.3</td>
</tr>
<tr>
<td>Decane</td>
<td>0.93</td>
<td>6.6, 16(39%), 10.3</td>
<td>9.5</td>
<td>10.8, 27(10%), 12.4</td>
<td>8.5, 25(28%), 13.1</td>
<td>2.3</td>
<td>10.4</td>
<td>2.3</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>2.5</td>
<td>9.9, 29(63%), 21.8</td>
<td>20.6</td>
<td>15.6, 30(60%), 24.2</td>
<td>13.5, 31(67%), 23.2</td>
<td>2.3</td>
<td>10.4</td>
<td>2.3</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>0.22</td>
<td>4.1, 29(65%), 20.0</td>
<td>26</td>
<td>24</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
</tr>
</tbody>
</table>

Viscosity $\eta$ (in cP), times $\tau$ (in ps), barriers (in cm$^{-1}$). Band decay after 0.5 ps is biexponential, $a_1 \exp(-\tau_1/\tau) + a_2 \exp(-\tau_2/\tau)$ with $a_1 + a_2 = 1$, and $\tau_\text{av} = (a_1 \tau_1 + a_2 \tau_2)$ is the average slow time. In the case of trans, a fast component $\exp(-\tau_1/\tau)$ has $\tau_1 = 0.3$ ps for SE$_{350}$ and 0.4 ps for ESA$_{550}$, ESA$_{420}$ and bleach. In the case of cis, $\tau_1 = 0.06$ ps for all bands except bleach. Central wavelengths are indicated and assignments (or labels as in Figures 2 and 6) are given in parentheses.

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path. The 14 ps decay of cESA corresponds to the excited-state lifetime of c-stiff. Kinetics in acetonitrile are displayed in Figure S6. The ultrafast oscillatory component is again very prominent and close to what is observed in hexane. However the slow evolution proceeds with 2 ps, much faster than in hexane. Interestingly, in acetonitrile the decay of t-stiff occurs also with 2 ps, so in this solvent the cis-to-trans and trans-to-cis isomerization rates are the same.

3.3. Raman Spectra and Kinetics. FSR spectra of t- and c-stiff in hexane are shown in Figure 10, left. S1 spectra are obtained by averaging over 0.1−0.5 ps, following UV actinic excitation at 340 nm for t-stiff and at 351 nm for c-stiff. On the right in Figure 10, the Raman spectra of stiff are compared to those of the parent stilbene. The comparison reveals many common features. For example in the ground state S0, Raman activity is strong in the high frequency range and very weak at
low frequencies for both compounds. The prominent bands around 1600 cm$^{-1}$ are nearly coincident. $S_1$ Raman bands are broadened compared to those in $S_0$, but for t-stilbene, the broadening is larger compared to t-stilbene, in agreement with a shorter excited-state lifetime. The C=C stretching mode of the central double bond at 1500 cm$^{-1}$ is shifted down by 70 cm$^{-1}$ compared to that of t-stilbene.

Switching to cis $S_1$ spectra, note that in this case Raman lines are broader for c-stilbene, reflecting its shorter lifetime compared to c-stilbene. In the low frequency range the modes about 200 and 300 cm$^{-1}$ are nearly coincident and equally intense for the two compounds. In the high frequency range, however, Raman activity of c-stilbene is very weak, whereas c-stilbene reveals intense bands about 1500 cm$^{-1}$. Interestingly, these bands are short-lived as seen from their kinetics in Figure 11. Thus the long-time spectra ($t>1$ ps) of c-stilbene and c-stilbene are very similar. Raman $S_0$ and $S_1$ frequencies are given in the SI.

Some Raman kinetics of t- and c-stilbene in hexane are displayed in Figure 11. Generally, they mirror the behavior of the TA kinetics discussed above. A 190 cm$^{-1}$ mode of t-stilbene reveals a rising component that may reflect the early adiabatic trans-to-cis isomerization (cf. Figure 2). Also, strong oscillations and decay of c-stilbene high-frequency modes (at 1200 and 1500 cm$^{-1}$) reproduce the TA behavior of SE and ESA bands shown in Figure 8.

3.4. Potential Energy Surface (PES). Let us begin to rationalize our experimental observations in terms of an effective one-dimensional potential energy scheme, as shown in Figure 12. Here the reaction coordinate $\theta$ is the torsion angle around the central C=C bond, starting from the trans isomer $\theta=0$. Population in $S_1$ is monitored by SE (optical transition $S_1 \rightarrow S_0$) and ESA ($S_1 \rightarrow S_n$). Its motion along the $S_1$ curve changes the transition energies which are being sampled, resulting in dynamic shifts of SE and ESA bands. Shifts are larger for SE than for ESA since the gradient of $(S_0 - S_1)$ is larger than that of $(S_1 - S_n)$. Finally the population drops to the ground state, via an $S_0/S_1$ conical intersection seam which opens up close to the perpendicular ($\theta=90^\circ$) geometry $P$.

Consider first the trans-to-cis path. Optical excitation creates population at point A which lies higher than barriers A1 and B1. A minor part of the population may overcome A1, rush through the perpendicular geometry and may reach, over barrier B1, the
bands (see Figure 8).

independent. The rest of population equilibrates around $A_0$ and
region, to be trapped there. This initial evolution is viscosity-
trans-to-cis isomerization. Also for c-stilbene, strong oscillations and fast decay of high-frequency Raman modes mirror the behavior of its SE and ESA bands (see Figure 8).

Figure 11. Evolution of selected Raman bands of t-stilbene and c-stilbene in hexane. Biexponential fit parameters ($\tau_1, \tau_2$ in ps) are shown as inserts. Generally the behavior of Raman and TA kinetics is similar. A 190 cm$^{-1}$ mode (top left) of trans reveals a rising component that could reflect early adiabatic trans-to-cis isomerization. Also for c-stilbene, strong oscillations and fast decay of high-frequency Raman modes mirror the behavior of its SE and ESA bands.

Figure 12. Schematic PES of stiff-stilbene in hexane. Torsion is the main reaction coordinate although the path is in fact multidimensional. Starting from trans (A) relaxation to $A_0$ should be seen as an ultrafast shift of tESA, but this process is not resolved. However the late (diffusive) stage of this relaxation is visible as a red-shift by 10 nm with 0.7 ps. A is located higher than $A_1$ and $B_1$, therefore a part of excited population overcomes $A_1$ ($E_{A_1} \sim 400$ cm$^{-1}$), passes through the perpendicular conformation ($P$) and reaches, within 0.3–0.4 ps, the cis region, to be trapped there. This initial evolution is viscosity-independent. The rest of population equilibrates around $A_0$ and experiences thermally activated viscosity-dependent decay to $P$ with 5 ps. At the same time the trapped cis population relaxes to $P$ over $B_1$ ($E_{B_1} \sim 800$ cm$^{-1}$) with 13 ps. The complexity of evolution explains multiple relaxation time scales of the trans isomer. For the cis-to-trans reaction, torsion starts in point $B_1$ close to the height of $B_1$ and $A_1$. A part of population overcomes barriers $B_1$, $A_1$ to reach the trans conformation, the rest thermally decays to $P$ with 13 ps.

cis conformation. It is trapped there to live slightly longer than the major part of the population which relaxes to the trans conformation. This early evolution, with characteristic time $\tau_1 = 0.3–0.4$ ps, is viscosity-independent and faster for tSE than for tESA. The independence on viscosity can be explained by assuming solvent collision time to be comparable or longer than $\tau_1$. In this case the motion during $\tau_1$ (between two successive collisions) is governed by intramolecular forces only and is therefore viscosity-independent. The discrepancy between tSE and tESA decays is probably due to a different dependence of their oscillator strength $f(\theta)$ on torsion angle $\theta$. An area were $f(\theta)$ is large is called the Franck-Condon (FC) region for the pertinent electronic transition. This area around $A_1$ is apparently larger for tESA than for tSE, partly due to stronger variations of the $S_n$ potential energy compared to $S_0$. Hence the tSE FC region is left faster than that of tESA, or tSE vanishes faster than tESA.

The next important point is that the growth of cESA (the small rising band in Figure 2) mirrors the decay of tESA exactly. That is, after leaving the trans FC region around $A_0$, population appears in the cis FC region $B_0$ practically immediately, i.e., within our time resolution. This suggests that the time necessary to pass $A_1B_1$ is less than 0.1 ps, otherwise a delay between the decay of tESA and the growth of cESA would be detected. Motion along $A_1P$ and $PB_1$ is unobservable (dark) and ultrafast. The population becomes visible again when it reaches other FC regions, first around $P$ and then around $B_1$.

Until now we have considered only the fastest relaxation stage, of population that has enough energy to overcome the $A_1$ barrier. The rest equilibrates about $A_0$ and experiences thermally activated viscosity-dependent decay to $P$ with time $\tau_{av} = 2–8$ ps (Table 1). The energy $E_{A_1}$ of the $A_1$ barrier can be estimated from $E_{A_1} = k_BT \ln(\tau_{av}/\tau_0)$, with $T = 294$ K, $k_B T = 204$ cm$^{-1}$. Here $\tau_0 \sim 0.2$ ps is an estimate of the barrierless isomerization time, and $\tau_{av}$ is the tESA decay time from Table 1. This gives $E_{A_1} = 650$ cm$^{-1}$ in hexane and 460 cm$^{-1}$ in acetonitrile.

The cis-to-trans reaction is considered next. In this case the interpretation is complicated by the strong band X (Figure 6, top right) which, at very early time, covers the range around 550 nm where a small rising tESA band is expected. The photoreaction starts from point B which is higher than $A_0, B_1$. A part of the population could overcome $B_1$, $A_1$ and reach the trans conformation. However, because of the aforementioned
spectral overlap, the corresponding ESA band cannot be identified in the transient absorption spectra directly. Instead one has to turn to the kinetics at later time when the initial relaxation is over; an excited trans population could be indicated by the kinetic signatures in Table 1. Namely, transient absorption at 550 nm decays in hexane with 8.8 ps, faster than cESA (12.7 ps on average). The decay of ESA at 650 nm by itself is biexponential, \( t_2 = 4.9 \) ps (15%), \( t_3 = 13.9 \) ps, pointing to 15% of trans component. The major part of population equilibrates about \( B_0 \) and experiences thermally activated decay to 15% of trans component. The major part of population with calculations of Liu Morokuma and with our own calculations of \( S_1 \) trans-isomer to be ca. 0.1 eV more stable than the cis one and \( S_0 \) cis to relax to the same A-symmetric \( S_0 \) state. Regarding the observation of \( t_{SE} \) shifting from 350 nm to 460 nm, it is attributed to the initial \( B \to B_0 \) relaxation. We will come back to this important point later.

4. COMPUTATIONAL RESULTS

Unlike parent stilbene, where some controversy remains regarding molecular planarity in the electronic ground state,\(^{28,37}\) steric interactions of the stiff methylene moieties, either with each other (cis) or with central ethylenic hydrogens (trans), allow for the \( C_2 \) symmetry only. We calculated the trans-isomer to be ca. 0.1 eV more stable than the cis one and that the vertical transition the \( S_1 \) state is 4.15 eV (oscillator strength \( f \sim 1.0 \)) in trans and 4.06 eV (\( f \sim 0.6 \)) in cis. These transition energies are 0.3–0.4 eV higher than the TDDFT data\(^{8}\) which are in better agreement with experiment. Perhaps a triple-\( \zeta \) basis set would enable a more accurate description of the excitation energy, but presently this is prohibitively expensive for stiff-stilbene. Calculated energies are collected in Table 2.

<table>
<thead>
<tr>
<th>Table 2. Calculated ( S_0 ) and ( S_1 ) Energies of Stiff</th>
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<tbody>
<tr>
<td>( \text{energy, eV} )</td>
</tr>
<tr>
<td>t-stiff, ( S_0 )</td>
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<tr>
<td>c-stiff, ( S_0 )</td>
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<tr>
<td>t-stiff, ( S_1 ) vertically excited</td>
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<td>c-stiff, ( S_1 ) vertically excited</td>
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<td>c-stiff, ( S_1 ) stationary point</td>
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<tr>
<td>c-stiff ( S_1 ) isomerization barriers</td>
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<tr>
<td>perpendicular-pyramidalized stationary points in ( S_1 )</td>
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</table>

In agreement with Improta and Santoro,\(^{8}\) but in contrast with calculations of Liu Morokuma\(^{25}\) and with our own experiment, we find no barrier for the excited trans-isomer. CASCCF with sufficiently large active spaces\(^{18}\) has a tendency to overestimate the barrier in trans-stilbene while CASPT2 and LR-TDDFT clearly underestimate it. Possibly we see the same effect in stiff where an even lower barrier, <0.1 eV, completely disappears at the TDDFT\(^8\) and XMCQDPT2 levels of theory. Interestingly, CASCCF\(^{25}\) does not capture the barrier on the cis side, which was observed in our experiment and calculations as well as in earlier calculations.\(^8\)

A fast component of trans-to-cis conversion before vibrational relaxation, as speculated in section 3.1, is consistent with our calculations. The initially excited trans-isomer has excess internal energy of 0.5 eV over the barrier between the cis and \( P \) state. Regarding the observation of \( t_{SE} \) shifting from 350 nm to about 400 nm within 0.3 ps (Figure 2b): this is in agreement with the computational result that considerable \( S_1 \to S_0 \) oscillator strength exists over a broad range of twisting angles. It is only upon twisting by 60° from the trans-configuration that the initial oscillator strength of the transition becomes halved. Moreover, this decrease in intensity is partly due to the narrowing of the \( S_0 \to S_1 \) gap to 2.5–2.7 eV rather than due the transition dipole moment; hence the shift.

Next let us consider the cis isomer. In its \( S_1 \) state the stationary point retains the \( C_2 \) symmetry (Figure 13a).

Redistribution of bond lengths and increase of the central twisting angle (C(arom)-C(et)-C(et)-C(arom)) to 40° provides relaxation by 0.54 eV compared to the vertically excited point. Accordingly the \( S_0 \to S_1 \) gap shrinks to 2.80 eV for cis-stiff, in agreement with the position of the broad SE band after its early evolution, with a drop of the SE oscillator strength from 0.6 to 0.4. We find no other energy minima, neither in the cis domain of \( S_1 \) nor in \( S_2 \) and \( S_3 \). The two latter states were found to relax to the same A-symmetric \( S_2 \) that descends to the perpendicular geometry. There \( S_2 \) forms asymmetric stationary points upon interaction with \( S_1 \), thus exhibiting sudden polarization analogous to parent stilbene.\(^{28}\) The effective Löwdin charges on the central ethylenic carbons reach nearly -0.4e on the pyramidalized side and +0.4e on the planar side while the adjacent phenyl moieties bear additional -0.2e and +0.2e, respectively. Importantly, unlike in parent stilbene,\(^{28}\) we observe two distinct asymmetric stationary points for the perpendicular state. Both of them are characterized by pyramidalization of one of the central carbon atoms but differ in its direction (Figure 14). Their energy differ by only 0.07 eV.
and the lower of them is located 0.7 eV below the vertically excited cis- and trans-isomers and 0.2 eV below the cis-stationary point in the S1 state. Unfortunately we were unable to locate the S1/S0 intersections at the XMCQDPT2 level due to the high number of molecular degrees of freedom. However note that at the perpendicular-pyramidalized stationary points of S1, the energy gap (S0−S1) is rather low (ca. 0.8 eV) and the gradient in S0 relatively large. These observation suggest, in analogy with our findings for unsubstituted stilbene,28 that the minimum energy crossing point will be close to the said stationary points both in terms of energy and geometry.

The calculated barriers from the excited cis-isomer to the perpendicular-pyramidalized stationary points, 300 cm⁻¹ to the lower and 680 cm⁻¹ to the higher lying one, are also in agreement with the experimental data. The transition state geometries are characterized by a minor degree of pyramidalization and by general asymmetry. Therefore the principal reaction coordinate is the anticipated twisting around the central bond, the twisting angle reaching 60° for the lower of the two barriers. Intriguingly, there are indications in the calculations that the minimum energy path from the trans-isomer leads to the second, higher-lying pyramidalized conformation.

5. IMPLICATIONS FOR PARENT STILBENE

It is interesting to compare the photoinduced evolution of stilbene with that of parent stilbene. In particular, does an S1 adiabatic passage between the two isomers (cis-to-trans or trans-to-cis) take place in the unmodified stilbene molecule?

TA spectra of cis and trans-stilbene in hexane, scaled to an equal excited-state population, are displayed in Figure 15. Isomerization of c-stilbene (left) is recognized from decay of a cESA band peaked at 632 nm, and from rise and subsequent decay of a P band around 320 nm (associated with the perpendicular conformation). The cESA decay is biexponential, r1 = 0.23 ps, a1 = 0.16, r2 = 0.9 ps; so the major evolution is complete on a 1 ps time scale. Switching to the trans spectra (top right), one observes a very intense tESA band at 582 nm, which is blue-shifted and 5–6 times stronger than the cESA band. Therefore, if a cis-to-trans adiabatic transition were real, then the tESA band would be clearly visible in cis transient spectra. However, the experimental spectra show no sign of that band, hence the cis-to-trans adiabatic passage does not occur.

Now consider the opposite trans-to-cis transition. Early spectra of t-stilbene (t < 1 ps, top right) reveal subtle changes which are better visible upon subtraction of a 0.12 ps spectrum (bottom right). One can distinguish the decay of tESA and the growth of the P band about 320 nm, as well as an increase of signal in the cESA region. This may be an indication of excited cis species. Late spectra of t- and c-stilbene (Figure 16) provide some support for this viewpoint. Indeed, the trans spectrum at 600 ps shows absorption in the range 400–600 nm. There is apparently a contribution to this signal from the tESA band (between 550 and 600 nm). Upon correction to this contribution, the residual signal resembles well the DHP band observed with c-stilbene. Thus the trans-to-cis adiabatic passage looks probable. Interestingly, the observed asymmetry, regarding S1 cis—trans versus trans—cis path, quite contradicts the fact that vertically excited cis-stilbene has 0.3–0.4 eV higher energy than the trans-isomer. Moreover, according to computations28 the isomerization barrier on the cis-side is 0.1–0.2 eV lower than that on the trans-side.

We summarize the picture of stilbene evolution, using the potential energy scheme of Figure 17. When starting from trans (A), a tiny fraction of excited population, having enough energy to overcome A1 (E(A1) ≈ 1230 cm⁻¹ in hexane and 1080 cm⁻¹ in acetonitrile), reaches P and subsequently the cis conformation. The rearrangement takes 0.2–0.3 ps similar to stil-stilbene. This early evolution is reflected in the transient difference spectra (Figure 15, bottom right). Afterward the cis population goes back to P over a lower B1 barrier (E(B1) ≈ 300 cm⁻¹ in hexane and 180 cm⁻¹ in acetonitrile) and finally decays to the ground state through S0/S1 conical intersections. Note that computations predict the B0 minimum of stilbene to be relatively deep (and the B1 barrier, accordingly, much higher) and to have DHP rather than cis-stilbeneic character.19,28 However, the evolution is rapid enough, which prevents the dominant part of the excited ensemble from being trapped in the DHP well upon energy loss.

The major trans population of excited stilbene equilibrates around A0 and experiences thermally activated decay to P. The decay is monoeXponential, with t = 84.2 ps (at 20.5 °C) when measured from the tESA or bleach evolution, and with t = 79 ps when measured from the tSE decay. This % discrepancy in decay reflects in our opinion the difference of tESA and tSE Franck−Condon regions, similar as in trans-stiff. When starting from cis (B) a substantial part of population overcomes the low B1 barrier within 0.2–0.3 ps, while the rest equilibrates around B0 and decays to P with 0.9 ps by thermal activation; in this way the biphasic behavior of c-stilbene in solution can be explained.
6. DISCUSSION

The first result of this paper is the existence of an adiabatic trans–cis (and possibly, cis–trans) passage on the $S_1$ energy surface. This aspect of the excited-state evolution is unusual, although it was anticipated in calculations and postulated by Saltiel and co-workers in their stationary fluorescence study of cis-stilbene. In more recent studies, such an effect has not been reported however; therefore it is necessary to consider alternative scenarios.

Figure 15. TA spectra of c- and t-stilbene in hexane at 20.5 °C. Upper panels show the signal from −0.06 to 0.12 ps. After $t = 0.06$ ps cESA at 634 nm slightly shifts to the blue, while tESA at 582 nm reveals no shift. Thus like in t-stiff, the early relaxation of t-stilbene is not resolved. Isomerization of c-stilbene is seen as decay of cESA and rise of P at 340 nm. The cESA decay is biexponential, $\tau_1 = 0.23$ ps (16%), $\tau_2 = 0.9$ ps. The perpendicular state P decays with 0.3 ps via $S_1/S_0$ conical intersection to hot c- and t-species and DHP. The evolution of t-stilbene ($0.12 < t < 1$ ps) reveals subtle changes, which are better visible upon subtracting a 0.12 ps spectrum, as shown at the bottom right. One can distinguish the decay of tESA and formation of P and cESA.

Figure 16. Late TA spectra of c-stilbene and t-stilbene in hexane. At 600 ps the trans spectrum shows traces of DHP (lower frame with expanded y-scale), indicating that cis species have been created in the excited state.

Figure 17. Stilbene PES in n-hexane. When starting from A (trans), a fraction of excited population has enough energy to overcome $A_1$ ($E_{A1} \approx 1250$ cm$^{-1}$) and reach the cis conformation. The rearrangement takes 0.2–0.3 ps as seen from TA spectra of Figure 15 (middle and bottom right). The cis population relaxes back to P over B$_1$ barrier ($E_{B1} \approx 300$ cm$^{-1}$) and then to the ground state. The major trans population equilibrates around A$_0$ and thermally decays to P with $\tau = 84$ ps. When starting from B (cis) a part of population overcomes B$_1$ within 0.2–0.3 ps; the rest equilibrates around B$_0$ and decays to P by thermal activation with 0.9 ps, in agreement with experimentally observed biexponential behavior in solution. For example for t-stiff one may speculate that the 0.3–0.4 ps spectral evolution reflects A $\rightarrow$ A$_0$ relaxation (see Figure 12) where A$_0$ is displaced, say, by 20–30° from the plane...
The disappearance of Raman activity in the 1500 cm⁻¹ range is discussed next. The electronic change is accompanied by the unidirectional ultrafast component.

The first result concerns the early transient spectra of c-stiff which, intriguingly, look similar to those of t-stiff. More precisely, the initial excited-state absorption band X of c-stiff has shape and position like tESA. A qualitative explanation of this surprising fact is essentially based on the molecular stiffness, which results in similar electron delocalization for both isomers. This is in agreement with our calculations (Table 2) which predict close S₀ → S₁ transition energies. Therefore, just upon S₀ → S₁ excitation when the ground-state geometry is still preserved, one may expect that S₁ → S₀ transition energies are close as well. Thus X is assigned to excited-state absorption from a region around the cis FC geometry (B₀ in Figure 12).

The ultrafast (0.06 ps) oscillatory component reflecting the transition from the initial band X to the “usual” cESA band is discussed next. The electronic change is accompanied by the disappearance of Raman activity in the 1500 cm⁻¹ range. We believe that the oscillation is related to motion of the ethylenic methylene. In this connection we studied the photoisomerization of 1,1’-difluorostilbene. In that molecule the cis isomer strongly resembles c-stiff, namely its excited-state evolution shows similar ultrafast decay and oscillations. The similarity is not accidental and may help to understand the nature of the ultrafast component.

We would like to mention another (improbable but enticing) explanation of the early c-stiff evolution. Imagine that the initial torsion from the cis geometry is so fast that molecules reach the trans conformation within 0.1 ps and continue their motion in the same direction. Then the early spectra and their evolution can be explained: early tSE and tESA would be observed simply because molecules have arrived at the trans configuration within our time resolution. At this point and time, the torsional motion would have slowed down, but it could still be fast enough to result in the observed 0.06 ps decay of the generated tESA band. In this case the oscillatory recurrence of X would indicate a recurrence of the trans configuration in the course of unidirectional torsion. Unfortunately, this attractive picture is probably wrong. An estimate of the energy gradient and moments of inertia shows that cis-to-trans torsion time is τ₀ ∼ 0.1 ps and must be resolved in our experiment. That is, cis bands should appear first followed by trans ones.

In connection with the above, an interesting question is how fast barrierless torsion can be. For stilbene and stilbene-like molecules τ₀ = 0.2 ps is experimentally established and in agreement with our computational estimate. τ₀ sets a useful time scale when looking for isomerization barriers and, more generally, for understanding intramolecular processes.

Switching to parent stilbene, we already mentioned that Saltiel and co-workers discussed the possibility for an adiabatic cis-to-trans isomerization of c-stilbene in S₁. The hypothesis can easily be checked with the spectra of Figure 15. Remember that tESA at 582 nm is much stronger than cESA at 634 nm; in addition there exists intense tSE about 350 nm. Hence an adiabatic appearance of t-stilbene should be quite visible, both by excited-state absorption at 582 nm and by stimulated emission at 350 nm. However, Figure 15 provides no sign of such bands. We conclude that the cis-to-trans isomerization does not occur in the excited state of stilbene. But the opposite trans-to-cis reaction does indeed take place, as seen from trace of DHP products (Figure 16).

The third result follows from the viscosity dependence of the isomerization time of t-stiff and t-stilbene, as compared in Figure 5. The two dependencies are rather similar, which implies a common isomerization mechanism. Although for t-stilbene the C=C torsion is usually considered to be the S₁ reaction coordinate, there are reports which propose a Hula-twist mechanism for stilbene isomerization. The phenyl moieties would hardly move during the Hula-twist process, and consequently the viscosity dependence is expected to be weak, contrary to observations with stilbene. Here t-stiff plays an important role as reference molecule, because it can be assumed with confidence to follow the torsion pathway exclusively. The same comparison can be used to clarify the isomerization pathway in other compounds. For example, azobenzene shows very weak viscosity dependence of its isomerization time, thus favoring the Hula-twist mechanism.

7. CONCLUSION

Stiff-stilbene was designed originally so that the well-known photoisomerisation of stilbene is channeled along the torsional pathway. The chromophor has been used as key element in molecular (unidirectional) rotors and as a molecular force probe. But apart from such applications, stiff-stilbene also provides a useful reference for spectroscopic changes which accompany the photoisomerisation of stilbenoid systems. It is for this reason that we re-examined the photoisomerization dynamics of stiff-stilbene in solution by broadband transient absorption and Raman spectroscopy and with quantum-chemical calculations. We find:

An adiabatic trans—cis pathway exists on the S₁ potential energy surface, allowing a fraction of excited trans molecules to bypass the conical S₁/S₀ intersection at the perpendicular geometry. A similar possibility appears to exist for excited trans-stilbene.

Upon excitation of cis, the S₁ Franck—Condon state has a pronounced excited-state absorption band at 550 nm and shows Raman activity in the 1500 cm⁻¹ C=C stretch region. These properties differ substantially from those of excited cis-stilbene. The FC state relaxes to a local cis minimum in 60 fs.

Isomerization rates of trans-stiff and trans-stilbene are affected similarly by microviscosity, pointing to the same S₁ reaction coordinate, torsional change.

More generally, by comparing the spectral evolution of substituted stilbenes with that of parent stilbene, specific differences or similarities may be identified for quantum-chemical calculations at a high level. Using this approach we discovered new aspects of stilbene photochemistry, and therefore it will be followed in our laboratory.

ASSOCIATED CONTENT

Supporting Information
Stationary absorption and fluorescence spectra, transient absorption spectra and kinetics, as well as Raman spectra and kinetics together with experimental and calculated vibrational wavenumbers, calculated molecular geometries and isomerization yield data are collected in the Supporting Information.
This information is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

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