Time-Resolved Photochemistry of Stiffened Stilbenes

Olivia A. Krohn,[†] Martin Quick,^{*,‡}[●] Ilya N. Ioffe,^{*,§} Olga N. Mazaleva,[§] Dieter Lenoir,[∥] Heiner Detert,[⊥] and Sergey A. Kovalenko[‡]

[†]Department of Physics and Department of Chemistry, University of Colorado, Boulder, Colorado 80309-0215, United States

[‡]Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, D-12489 Berlin, Germany

[§]Department of Chemistry, Lomonosov Moscow State University, Moscow 119991, Russia

^{II}Helmholtz Center München, Postfach 1129, 85664 Neuherberg, Germany

¹Institute for Organic Chemistry, Johannes Gutenberg-University Mainz, Duesbergweg 10-14, Mainz 55099, Germany

Supporting Information

ABSTRACT: Broadband transient absorption spectroscopy is used to study the photoisomerization of stiffened stilbenes in solution, specifically E/Z mixtures of bis(benzocyclobutylidene) (t4, c4) and (E)-1-(2,2-dimethyltetralinylidene)-2-2dimethyltetraline (t6). Upon excitation to S_1 , all evolve to perpendicular molecular conformation P, followed by decay to S_0 , while the spectra and the kinetic behavior crucially depend on the size of the stiffening ring. In 4, contrary to all previously studied stilbenes, the trans and cis absorption and excited-state spectra are nearly indistinguishable, while the corresponding isomerization times are comparable: $\tau_i = 166$ ps for t4 and τ_i = 64 ps for c4 in *n*-hexane, as opposed to 114 and 45 ps in acetonitrile, respectively. Faster isomerization in polar solvents agrees with the zwitterionic



character of the P state. In t6, torsion to P is effectively barrier-less and completes within 0.3 ps, the $S_1 \rightarrow P$ evolution being directly traceable through the transient spectra of stimulated emission and that of excited-state absorption. In n-hexane, the P state is remarkably long-lived, $\tau_{\rm p}$ = 1840 ps, but the lifetime drops down to 35 ps in acetonitrile. The trans-to-cis photoisomerization yield for t6 is measured to be 20%, while for t4, it remains uncertain. We discuss the effects of stiffening and substitution on the formation and lifetime of the intermediate states through which the stilbene molecules evolve on the S_1 energy surface.

1. INTRODUCTION

The general trends in photodynamics of symmetric stilbenes have been elucidated in several experimental¹⁻¹³ and theoretical¹²⁻²⁰ studies. Normally, after initial excitation and rapid relaxation of high-frequency vibrational modes, both the cis and trans isomer undergo twisting around the central ethylenic bond. Eventually, they arrive to the perpendicular, spontaneously polarized domain of S₁ (a.k.a. "phantom state", P) and then return therefrom to S_0 . However exact details of the above evolution vary with the substitution. For example, there may be a barrier for twisting to P, whose lifetime ranges from femtoseconds⁴⁻⁶ to hundreds of picoseconds.⁷⁻¹¹

Stiffened stilbenes^{1,21–23} shown in Scheme 1 retain the π system topology of unsubstituted stilbene (t0) while eliminating the rotational degrees of freedom of the phenyl rings. Previously, we reported¹⁰ the photochemistry and photodynamics of trans- and cis-1,1'-bis(indanylidene) (t5, c5), the molecule with potential applications in molecular force probing²⁴ and light-driven nanomotors.^{14,25} Upon optical excitation to S_1 , t5 isomerizes to P with a 5 ps time, over a 10 kJ/mol barrier in *n*-hexane;¹⁰ however, quantum chemical calculations, with XMCQDPT2 multiconfigurational quasidegenerate second-order perturbation theory, show no barrier. In c5, with its 12 kJ /mol twisting barrier, the agreement

Scheme 1. Compounds under Study (t4, c4, t6) and Previously Studied (t5, c5)



between the experiment and the theory is better. Here, it is worth noting that the P state lives too short to be captured, in contrast with cis-stilbene c0 where the P state with a lifetime of 0.3 ps is well observed after the virtually barrier-less twisting.⁴

In the present paper, we extend our stationary and femtosecond broadband transient absorption study to two "cousin" molecules: (E/Z)-bis(benzocyclobutylidene) and (*E*)-1-(2,2-dimethyltetralinylidene)-2-2-dimethyltetraline (t4, c4, and t6, respectively). Smaller stiffening rings in t4 and c4

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diminish the steric interactions between the two halves of the molecule, whereas the dimethyl substitution in t6 provokes high sterical strain for the olefinic junction. Therefore, the type of the stiffening ring crucially influences the lifetime of various states in $S_{1,}$ as reflected in the transient photochemical behavior.

2. EXPERIMENTAL AND COMPUTATIONAL SECTION

2.1. Probe Molecules. The synthesis of compounds 4 and 6 was described in detail in refs 21, 23. Briefly, cis- and trans-(benzocyclobutenylidene)benzocyclobutene is obtained from benzocyclobutenone via the McMurry reaction following the procedure given by Oelgemöller.²¹ Zinc powder (2.8 g, 8.4 mmol) was added to a cooled (-10-0 °C) solution of TiCl₄ (1.62 mL, 15 mmol) in 150 mL anhydrous THF while stirring. After 15 min of stirring, benzocylobutenone (2.12 g, 12 mol) in 30 mL of abs THF was added dropwise, and the dark mixture was stirred under reflux for 26 h. The cooled mixture was added to 150 mL of 10% aqueous K₂CO₃ solution, and this mixture was extracted with 3×100 mL of ether and $2 \times$ 100 mL of petroleum ether. The combined organic layers were washed with water $(2 \times 100 \text{ mL})$ and brine (100 mL) and dried over MgSO₄, and the solvent was evaporated in vacuo. Purification by chromatography (cyclohexane/acetone = 10:1) gave a $\sim 2:1$ mixture of trans and cis isomers (1.03 g, 24%). The isomers were separated via repeated fractionating crystallization from solutions in chloroform, and 2-propanol was added until the solution became slightly turbid.

The synthesis of *E*-I-(3,4-dihydro-2,2-dimethyl-1(2*H*)-naphtalenyliden)-1,2,3,4-tetrahydro-2,2-dimethylnaphthalene is described in ref 23. A solution of 2,2-dimethyl-1-tetralone (2.26 g, 13 mmol) in 15 mL of THF was added to a mixture of TiCl₄ (1.6 mL) and Zn powder (2 g) in 110 mL of THF, as described above for t4/c4. The stirred mixture was refluxed for 26 h, cooled, and hydrolyzed with 10% aq. K₂CO₃, and the product was isolated by extraction with MTBE chromatography (light benzene/ether = 2:1), yielding 1.07 g (56%) colorless crystals, mp 193–194 °C.

Pure t4 and an E/Z mixture of 4 (~1:1 ratio from NMR) are measured upon 326 nm excitation. A second E/Z mixture (~1:1 ratio from NMR) is measured with TA, with 316 nm excitation this time. For pure t4, stationary and transient spectra should exhibit features from only the t4 isomer, while the two mixtures should yield spectra with contributions of the E and Z isomer. For compound **6**, the cis isomer is unstable at room temperature in solution and isomerizes to the more stable trans conformation within a few minutes.

2.2. Transient Absorption (TA). The experimental setup has been described elsewhere.^{10,26,27} In short, a Ti:Sa laser produces 40 fs, 500 μ J, and 500 Hz pulses at 800 nm. The majority of this, 420 μ J, pumps an OPA (optical parametric amplifier) to produce 50 fs and 2 μ J pulses at 316 nm. This pump beam has a spot size of 100 μ m and excites the sample. The rest of the fundamental is frequency-doubled and focused to a 1 mm CaF₂ plate to produce a supercontinuum probe. The supercontinuum is spectrally filtered and split into a signal and reference covering the spectral range of 275 to 690 nm. TA spectra are measured at 21 °C with parallel $\Delta A_{\parallel}(\lambda, t)$, perpendicular $\Delta A_{\perp}(\lambda, t)$, or magic-angle $\Delta A(\lambda, t)$ pumpprobe polarization. Transient anisotropy spectra $\rho(\lambda, t)$ are given as

$$\rho(\lambda, t) = (\Delta A_{\parallel} - \Delta A_{\perp}) / (\Delta A_{\parallel} + 2\Delta A_{\perp})$$
$$= (\Delta A_{\parallel} - \Delta A_{\perp}) / (3\Delta A)$$
(1)

Multiple pump-probe scans (8-16) are performed with 0.02, 0.4, 2, or 8 ps time steps. The resulting averaged TA spectra are time-corrected for the chirp of the continuum probe.²⁶

2.3. Data Analysis. A global kinetic analysis over the full TA spectra, with a sum of convoluted exponential time functions, is used to derive the time constants and amplitudes of the photoinduced relaxation processes. The joint sets of data with different time steps are comprehensively analyzed to ensure the resulting fits match each other. The results are visualized with band integrals

$$I(\lambda_1, \lambda_2, t) = \frac{1}{\ln(\lambda_2/\lambda_1)} \int_{\lambda_1}^{\lambda_2} \Delta A(\lambda, t) d\lambda/\lambda$$
(2)

calculated either directly from the experiment or from the corresponding global fit. When the spectral range (λ_1, λ_2) is carefully chosen, the band integrals improve the signal-to-noise ratio and eliminate the contributions from the spectral shifts. The integrals are fitted with exponentials to treat the evolution under study.

In the present case, we allow the fitted kinetics to contain a small (1-3%) contribution to ΔA from the anisotropy decay. This contribution is probably due to depolarization of the probe continuum by the CaF₂ plate (where the continuum is generated).

2.4. Calculations. Quantum chemical calculations are performed with the Firefly QC package version 8.2²⁸ partially based on the GAMESS (US) source code.²⁹ Ground-state geometry optimizations are done at the PBE0/Def2-TZVPP level of theory (TD-PBE0 is also used for preliminary reconnaissance of the S_1 potential energy surface). The excited state structures are optimized with the RI-XMCQDPT2 multistate multireference perturbation theory at the second order³⁰ with frozen chemical core. Unless specifically indicated, no symmetry is used in the calculations. For t4 and c4, we apply the larger basis set Def2-TZVP, while the smaller one, Def2-SVP, was used for t6. The CASSCF active space, the state-averaging scheme, and the XMCQDPT2 model space had to be varied between some of the computations, and their choice is described explicitly in each case. The intruder state avoidance (ISA) parameter is set to 0.02 au.

3. RESULTS

3.1. Calculated Ground-State Geometry. In the ground state, the four-membered stiffening rings in t4 and c4 are planar, and due to the ~90° valence angles, the halves of the molecule are spaced farther apart than in the previously studied t5 and c5. As a result, both t4 and c4 exhibit a perfect planarity and mirror symmetry in the ground state (C_{2h} and C_{2w} , respectively). The planarity of c4 constitutes a special case that is very different from other nonplanar *cis*-stilbenes.

In contrast, the bulky dimethylated six-membered stiffening rings in t6 do not allow planarity and give rise to several sterically strained conformations of both t6 and c6. The most stable conformation of t6 is characterized by the central dihedral angle of 148.5° and ~40° dihedral angles between the phenyl rings and the central ethylenic bond that makes the two rings nearly perpendicular (see the Supporting Information for coordnates). Interestingly, the most stable conformer of c6 is calculated to be only 27 kJ/mol higher than that of t6. The strong repulsion between the methylated stiffening rings in c6 is compensated by the stronger conjugation in the π system, in contrast to other stilbenes where the trans isomers show a higher degree of conjugation. The ground-state molecular geometries of t4 and t6 are shown in Figure 1. The calculated



Figure 1. Calculated ground-state geometries of t4 and t6.

geometries refer to the gas phase, and for the solid phase, X-ray structures has been reported,^{21,22} but we will refer to our calculated structures for our studies to be consistent.

3.2. Stationary Spectra. Extinction spectra of stilbenes 0, 4, 5, and t6 are displayed in Figure 2. Due to the higher



Figure 2. Extinction spectra of various stilbenes: t0, c0, t4, c4, t5, c5, and t6. A detailed description for the derivation of the c4 extinction spectrum is given in the text and the caption of Figure S1.

planarity of c4 and rigidity of t4, the spectra of the E and Z isomer, respectively, contain a sharp vibronic structure and, above that, are visually hardly distinguishable. A feasible separation into t4 and c4 extinction is performed on the late transient absorption (TA) spectrum. Here, the bleach region can principally be reconstructed by the difference extinction

spectrum of t4 and c4, $\varepsilon_{\rm c4}$ – $\varepsilon_{\rm t4}$, when only nonadiabatic trans-trans and trans-cis isomerization is considered. By adding the smallest reasonable amount of ε_{t4} to the TA spectrum, the appropriately scaled extinction of c4 eventually shows up. Moreover, the extinction spectrum of c4 can also be derived by stationary means from the t4/c4 mixture (~1:1 from NMR) by subtracting ε_{t4} with scaling factor f. The scaling factor f must be tuned until both c4 extinction spectra (stationary and from TA) coincide. The maximum amplitude within ε_{t4} (~70,000 cm⁻¹) is ~1.5 times larger than in ε_{c4} , which is a trend that is often observed for trans- and cis-stilbene and its derivatives. If another methylene unit is inserted to result in 5^{10} then a red shift of 1300 cm⁻¹ is observed for the $S_0 \rightarrow S_1$ absorption band, which possibly points to the higher conjugation for more relaxed valence angles. In addition, a slight drop in the amplitude is caused by broadening of vibrational bands, as compared to 4.

The vertical excitation energies in t4 and c4 are calculated at the XMCQDPT2 level of theory with the complete π orbital (14e,14o) active space, state-averaging over the six lowest CASSCF roots to cover the relevant contributions to the S_1 , and altogether 12 states in the model space (also see Section 3.4). Similar to t0,¹⁷ there are two appreciable transitions associated with unequal contributions of the HOMO¹LUMO¹ electronic configuration. In 4, the absorbing states are S_1 and S_3 that belong to the B_u representation in the C_{2h} symmetric t4 and to the B_1 representation in the $C_{2\nu}$ symmetric c4. The vertical transition energies are calculated to be 4.06 eV for S₀ \rightarrow S1 and 4.56 eV for S0 \rightarrow S3 in both t4 and c4. The calculated oscillator strengths are somewhat different, 0.74 for $S_0 \rightarrow S_1$ and 0.33 for $S_0 \rightarrow S_3$ in t4 versus 0.61 and 0.26 in c4, respectively. Also, almost equal are the estimates for the 0-0 transition obtained as the energy difference with the optimized S_1 (see below), 3.76 eV in t4 versus 3.77 eV in c4, the vertical emission energy being slightly more different: 3.62 eV in t4 versus 3.56 eV in c4. Thus, in agreement with the experiment, the absorption spectra of the two isomers coincide but could be distinguished by spectral intensities.

Comparing the calculated and measured spectra in Figure 2, note the calculated 0–0 transition agrees well with the first vibronic band. Unfortunately, determination of the center of gravity of the spectra for comparison with the calculated vertical transition is complicated by the overlapping $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_3$ bands. Perhaps, the weaker transition to S_3 is seen as the bumps around 36,000 cm⁻¹.

In t6, vibronic bands are not resolved anymore. The sixmembered ring allows for a larger structural variety with more low-frequency degrees of freedom and thus leads to wider spreading of the oscillator strength. A drop in extinction to $10,000 \text{ cm}^{-1} \text{ M}^{-1}$ goes along accordingly. Under illumination of t6, its absorption spectrum shows no change, indicating that eventually produced c6 isomerizes back to t6 within a minute. In agreement with those observations, XMCQDPT2 optimization of the t6-to-c6 minimum energy path in S₀ with the (10e,10o) active space and a single-state model space (thus effectively MR-MP2) arrives at a less-stable conformer of c6, which has the barrier for conversion to t6 of only 38 kJ/mol.

3.3. Photoisomerization Dynamics of t4 and c4. Generally, t4 reveals similar transient features as t0, while c4 differs in behavior from c0. TA spectra $\Delta A(\lambda, t)$ of t4 and c4 in *n*-hexane upon 326 nm excitation are displayed in Figure 3. The photoinduced evolution is similar in acetonitrile, therefore the following description also refers to that measurement.



Figure 3. Transient absorption (TA) spectra of t4 and c4 in *n*-hexane upon photoexcitation at 326 nm. Bleach and SE are negative, and excitedstate absorption (ESA) is positive; arrows indicate the signal evolution. After Franck–Condon (FC) relaxation, both t4 and c4 isomerize to P with specific time τ_i . A global analysis gives $\tau_i = 64$ ps for c4 and 166 ps for t4 in *n*-hexane and $\tau_i = 45$ ps (c4), 114 ps (t4) in acetonitrile. In the bottom left, t4 extinction ε_{t4} is added to reconstruct c4 extinction ε_{c4} . It follows that the c4 spectrum (in green) is blue-shifted by 1 nm with an amplitude ratio c4/t4 = 1:1.5; the t4 \rightarrow c4 isomerization yield being determined as $Y_{tc} = 20-30\%$. In the bottom right, the c4 \rightarrow t4 yield is estimated as 5– 20%.

Recall that excited-state absorption (ESA) is positive while stimulated emission (SE) and bleach enter the signal with a negative sign.

For t4, ESA rises at the early pump-probe delays, peaking at 516 nm in *n*-hexane (510 nm in acetonitrile). Franck–Condon (FC) initial relaxation proceeds within the first 0.6 ps, as seen by a redistribution of the oscillator strength in ESA and SE. The ESA decays within 300 ps, indicating the $S_1 \rightarrow P$ isomerization to the perpendicular conformation P. One exponential time constant is obtained by a global kinetic analysis: $\tau_1 = 166$ ps in *n*-hexane and $\tau_1 = 114$ in acetonitrile. These are consequently attributed to the trans isomer, in agreement with our calculations (see next section). The TA spectrum of pure c4 is isolated from the TA spectrum of coexcited c4/t4 by subtracting pure t4. The $S_1 \rightarrow P$ isomerization time, however, is withdrawn from the mixture by using two exponential time functions while fixing the time constant for t4. In *n*-hexane, c4 isomerizes with $\tau_2 = 64$ ps, and in acetonitrile, c4 isomerizes with $\tau_2 = 45$ ps.

Recall that, in c0, the $S_1 \rightarrow P$ isomerization in *n*-hexane proceeds with ~1 ps over a low barrier,^{4,5} while in c5, a barrier of 7.2 kJ/mol in acetonitrile (and 12.1 kJ/mol in *n*-hexane) prevents ultrafast isomerization.¹⁰ Probably, the repulsion between the phenyl rings is reduced with decreasing ring size (from c5 to c4), which forces the rings further apart. As a consequence, the isomerization barrier increases from 2 ps for c5 to the observed time $\tau_2 = 45$ ps for c4.¹⁰ The biexponential behavior in the E/Z mixture of 4 is visualized by the band integral I(410,690) shown in Figure 4 (bottom left). The TA signal (cyan) is well fitted by two exponentials ascribed to t4 (red) and c4 (blue).

The global analysis also gives species-associated spectra (SAS) of t4 and c4. These are shown in the right panels of Figure 4. The attribution follows from the separately measured t4 and from a general trend that the $S_1 \rightarrow P$ rearrangement is usually faster for the cis isomer. Worthy of note is the spectral resemblance between the SAS. The vibrational bands of the bleach signals are well resolved and coincide spectrally, which confirms the strict structural planarity in S_0 . The spectral



Figure 4. Results from a global analysis for pure t4 and c4/t4 mixture in *n*-hexane. Left: Band integral I(410,690) over the bleach band is shown (cyan), with faster decay τ_1 attributed to c4 (blue) and slower one τ_2 to t4 (red). Right: Species-associated spectra (SAS) from the global fit result in an E/Z ratio of ~1:1 in *n*-hexane and acetonitrile in agreement with the NMR results (~1:1).

similarity of t4 and c4 is further seen in their ESA bands shifted by 300 cm^{-1} only.

The E/Z ratio in S_0 can be deduced from the S_1 SAS in Figure 4, when the derived extinction spectra of t4 and c4 are taken as a basis. Recall that the oscillator strength of the S_1-S_0 transition is 1.5 times larger for t4. Due to the slight spectral shift between both isomers, the ratio $\varepsilon_{t4}/\varepsilon_{c4}$ at $\lambda_{exc} = 326$ nm is approximately 2:1. The calculated band integrals over the SAS bleach yield a ratio t4/c4 of ~3:1 (in both solvents) which, in the case of equal *E* and *Z* S_0 abundance, directly reflects the product of both the larger oscillator strength of t4 and its two times favored pumping into S_1 : 3/1 = 1.5/1 and 2/1. This finding is in agreement with the NMR results where an S_0 ratio of ~1:1 is determined. Note that this shift is not necessarily recognized in the bleach region of the SAS since the overlap with SE is strong for the 0–0 transition.

Returning back to the TA spectra in Figure 3, note that the bleach recovers with the same time constants as the ESA decay $(\tau_1 = 166 \text{ ps}, \tau_2 = 64 \text{ ps for } n\text{-hexane and } \tau_1 = 114 \text{ ps}, \tau_2 = 45$ ps for acetonitrile), indicating that the $P \rightarrow S_0$ transition proceeds much faster than the $S_1 \rightarrow P$ half-torsion. Late spectra at the bottom are recorded at 2 ns when the relaxation is complete. The residual bleach is small being \sim 5% of that at the early time (top). This suggests that either the t4 \rightarrow c4 yield is small or the yield is substantial but the extinctions of t4 and c4 are similar. Following the latter interpretation, the residual bleach cannot be perfectly reconstructed solely with the t4 extinction spectrum. In fact, little dispersive features hint for the c4 extinction spectrum being slightly blue-shifted. Adding the fewest possible amounts of ε_{t4} to the late TA spectrum eventually exposes the appropriately scaled c4 extinction spectrum, indeed being blue-shifted and with a maximum amplitude of 60% compared to t4. Knowing the extinction spectrum of c4 allows an alternative way of derivation. Therefore, the scaled ε_{t4} is subtracted from the measured joint extinction of t4 and c4 until the difference spectrum matches ε_{c4} from TA. The late TA spectrum left over from pure c4 contains a more pronounced dispersive bleach, with negative and positive parts being blue- and red-shifted. These band shapes consequently follow from the derived extinction spectra. Above 400 nm, the positive signal may indicate a triplet state; an alternative dihydrophenanthrene (DHP) relaxation channel common to many other stilbenes is prohibited in 4 because the four-membered stiffening rings keep the phenyl rings too far apart (see next section).

To calculate energy barrier E_b for $S_1 \rightarrow P$ or $P \rightarrow S_0$ halftorsion, the following estimate is applied

$$E_{\rm b} = kT \, \ln(\tau_i/\tau_0) \tag{3}$$

with kT = 2.44 kJ/mol at T = 21 °C. Here, $\tau_0 = 0.1$ ps is taken for barrier-less torsion (of the phenyl group). This value agrees with the isomerization rate of the parent stilbene,^{4,5} and it is assumed to be similar in the studied compounds. Such calculated isomerization barriers are collected in Tables 1 and 2.

3.4. Calculation Results on t4 and c4. XMCQDPT2 optimization of the excited t4 and c4 is carried out with a (10e,10o) CASSCF active space that included 10 π orbitals with the two lowermost occupied and the two uppermost

Table 1. Rotational Diffusion Time $\tau_{R'} S_1 \rightarrow P$ Isomerization Time $\tau_{i'}$ Barrier $E_{b1'}$ and Trans-to-Cis Isomerization Yield Y_{tc} in Various Stilbenes

stilbene	solvent	$\tau_{\rm R}~({\rm ps})$	τ_{i} (ps)	E_{b1} (kJ/mol)	$Y_{\rm tc}$
t0	<i>n</i> -hexane	14	84	16.7	0.50 ¹³
	acetonitrile	17	38	14.9	0.50
t4	<i>n</i> -hexane	14	166	18.1	
	acetonitrile	16	114	17.2	
t5	<i>n</i> -hexane	18	5	9.7	0.33 ¹⁰
	acetonitrile	22	2	7.4	0.33
t 6	<i>n</i> -hexane	16	0.1	0.0	0.25
	acetonitrile	22	0.1	0.0	0.25

Table 2. $S_1 \rightarrow P$ Isomerization Time τ_i , Barrier E_{b1} , and Cisto-Trans IsomerizationYield Y_{ct} and Y_{ccl} in Various Stilbenes

stilbene	solvent	$\tau_{\rm i}~({\rm ps})$	E _{b1} (kJ/mol)	$Y_{\rm ct}$	Y _{c cl}
c0	<i>n</i> -hexane	$0.23 \ (16\%), \ 0.91 \\ (84\%)^4$	5.2	0.50	0.05 ⁴
	acetonitrile	0.23 (27%), 0.48 (73%), ⁴ 0.75 ⁵	3.9, 5.0		
c4	n-hexane	64	15.8		
	acetonitrile	45	14.9		
c5	<i>n</i> -hexane	13 ¹⁰	12.1	0.33	0.05 ¹⁰
	acetonitrile	2 ¹⁰	7.4	0.33	

vacant ones left out. The HOMO¹LUMO¹ configuration that dominates the S₁ state is typically distributed over two or three B symmetric CASSCF roots (if C_2 symmetric geometry is considered). In our symmetry-less calculations, we use state-averaging over the six lowest CASSCF roots to cover the relevant contributions. The XMCQDPT2 model space includes the 12 states.

Similar to S₀, photoexcited t4 is found to be perfectly planar in S₁. The C₂ symmetric saddle point for twisting toward the P state is located at the central C(Ph)–C(Et)–C(Et)–C(Ph) dihedral angle of 138° (trans = 180°), and the barrier height is calculated to be 8 kJ/mol, a certain underestimation with respect to the experiment. Single-point recalculations with the (14e,14o) active space and with all 14 π orbitals result in an even lower value of 5 kJ/mol. The use of the C₂ symmetry and expansion of the model space to 30 B(B_u) symmetric states (with three-state averaging) produces only a marginally better estimate of 9 kJ/mol. It is worth noting that a similar underestimation was previously observed in stilbene¹⁷ and thus probably reflects the accuracy of the approach.

The excited c4, on the contrary, slightly deviates from the ground-state planarity, its central dihedral angle becoming 10.6°. The saddle point at 43.1° is calculated to be 4 kJ/mol above, so there is a consistent underestimation of the twisting barrier on both the cis and trans sides. Unlike c0 and c5,¹⁰ cyclization of c4 into a DHP-like molecule is unlikely as the relevant C…C distance is larger (3.9 Å vs 3.0 Å in c5) and the π -orbital axes of the respective two carbon atoms are nearly perpendicular to the interatomic vector.

Beyond the twisting barrier, within P, optimization reveals pyramidalization of one of the central C(Et) carbon atoms together with considerable stretching of the respective C(Et)-CH₂ bond. In order to properly account for the elongation effect, the active space is expanded to (12e,12o) including the σ -bonding and σ *-antibonding orbitals of the elongated bond. Interestingly, when still close to the twisting barrier, the processing pyramidalization required inclusion of the seventh CASSCF root into state averaging in order to encompass the major contributions to S₁. However, further evolution into the phantom state allows reduction to only two-state averaging and limiting of the XMCQDPT2 model space to six states only. It is found that P does not have any stationary point in S_1 as its minima coincide with the S_1/S_0 intersection sites, ~0.3 eV below the stationary points of t4 and c4 in S_1 . Thus, in agreement with the experiment, the P state must instantly relax to S_0 .

The two crossing points located can be distinguished by the direction in which the pyramidalizing C(Et) carbon points to. Apart from that, they share a similar structure and are

separated by 3 kJ/mol only. One of them is shown in Figure 5. Note that the sum of the three valence angles at the



Figure 5. Calculated P-state geometry $(S_1/S_0 \text{ intersection})$ of 4. The relevant angles and bond length are indicated.

pyramidalized center is ~293°, and the $C(Et)-CH_2$ bond is elongated to 1.85 Å. While in the course of geometry optimization, the dipole moment of P exceeds 10 D (and a quasi-lone pair forms at the pyramidalized site) but drops to 4 D in the direct vicinity of the crossing points.¹⁷

3.5. Photoisomerization of t6. TA spectra of t6 are recorded under the same experimental conditions (Figure 6). At the earliest delays, as the spectrum builds up, the SE band already starts shifting to the red (top). This shift indicates that the planar trans conformation is highly unstable in S_1 .

In both solvents, the early $S_1 \rightarrow P$ torsion progresses with <0.1 ps, indicating a barrier-less process. Band integrals are calculated over ESA and P absorption to visualize this evolution, (Figure 7). A strong and ultrafast red shift of SE should be ascribed to the decreasing $S_1 \rightarrow S_0$ transition frequency in the course of the wavepacket motion toward P. The SE band shifts from 400 to 550 nm (by 7000 cm⁻¹) and decays within 0.1 ps, while the red ESA band concurrently decays. Simultaneously, an ESA band from the P state emerges and peaks at 350 nm. The identification as P-ESA follows from the comparison with other stilbenes.^{4,6-11} The P state lives extraordinarily long in *n*-hexane, $\tau_P = 1840$ ps, while in acetonitrile, the lifetime shortens to $\tau_P = 35$ ps. A comparison of the P lifetimes in other stilbenes is given in Table 3.

Late bleach spectra, when all the population returns to S_0 , allow an estimate of the trans-to-cis isomerization yield Y_{tc} by comparing with the early bleach at t = 0.1 ps.⁶ For acetonitrile, this gives $Y_{tc} = 20\%$. Then, the c6 extinction spectrum can be reconstructed as shown by the orange lines in Figure 6 (bottom). In addition, a broad positive signal for $\lambda > 450$ nm indicates a phenanthrene-like photoproduct via ring closure in adiabatically formed c6. In *n*-hexane, a 20% photoisomerization yield is found again. Here, the full recovery of S_0 exceeds our time window of 2 ns. By enlarging the probe optical path manually, a TA spectrum at 8 ns was measured and used to estimate Y_{tc} . Note that no positive band emerges at $\lambda > 450$ nm; hence, no ring closure takes place in *n*-hexane. The photoisomerization barriers calculated with eq 3 are collected in Table 1.

3.6. Calculation Results on t6. The XMCQDPT2 calculations, with a (10e,10o) active space, seven-state



Figure 6. TA spectra of t6 in acetonitrile (left) and in *n*-hexane (right) upon photoexcitation at 316 nm. The initial evolution is ultrafast, $\tau < 0.1$ ps and includes the ESA decay, SE red shift and decay, and P rise at 350 nm (second frames). The P lifetime is extraodinarily long in *n*-hexane, $\tau_p = 1840$ ps, while it is much shorter in acetonitrile, $\tau_p = 32$ ps (third frames). At the bottom, late spectra (olive) allow derivation of the isomerization yield $Y_{tc} = 20\%$ and the cis spectra (orange).

averaging, and seven states in the model space, show that photoexcited t6 relaxes to P without a barrier, in agreement with the experiment. Unlike for 4, P here has a proper stationary point located at 1.45 eV below the vertical excitation. However, its geometry is significantly different from those calculated in t0 and $t5^{10,17}$ and from the crossing points in t4 and c4. While there is a pronounced desymmetrization between the halves of the molecule and the dipole moment exceeds 13 D, there is almost no pyramidalization in the P state. On the contrary, the S_1/S_0 crossing point is pyramidalized (see the Supporting Information) as in other stilbenes. The S_1/S_0 minimum energy crossing point is calculated to be 50 kJ/mol higher than the minimum of the P state. Compared to the experimental $P \rightarrow S_0$ barrier of 24 kJ/mol, this is a twofold overestimate due to, perhaps, a relatively scarce basis set. However, this increased relaxation barrier illustrates a trend that is discussed below.

4. DISCUSSION

First, we compared the TA results on **4** and **t6** with parent stilbenes **0** and **5**. For **t0** in *n*-hexane, the $S_1 \rightarrow P$ torsion occurs with $\tau_i = 84$ ps over barrier $E_b = 16.7$ kJ/mol. In acetonitrile, the barrier is reduced to $E_b = 14.9$ kJ/mol as the P state is zwitterionic and stabilized in polar solvents. The case of solvent-induced stabilization for **t0** and **t4** is schematically approached by diabatic potentials, as shown in Figure 8 (top).

While the trans and cis sites of S_1 in the Franck–Condon geometry are not affected by the solvent polarity, the potential of the P state lowers in acetonitrile. As a consequence, the intersection between the trans (or cis) isomer and P potential shifts toward the stationary point of the untwisted configuration, and the isomerization barrier E_b to P reduces. The subsequent transition to S_0 follows nearly instantaneously. Recall that, for c0, the $S_1 \rightarrow P$ isomerization barrier is strongly reduced ($E_b = 4$ kJ/mol in the experiment or no barrier in the computations), resulting in a fast $S_1 \rightarrow P$ transition with solvent-dependent $\tau_i = 0.4-0.9$ ps. For c4, this is not the case; the $S_1 \rightarrow P$ barrier remains high, contrary to what happens in other stilbenes.

The dependence of the P lifetime on solvent polarity is apparent in t6 and other substituted stilbenes^{6–8} and can be explained in Figure 8 (bottom). The aforementioned lowering of the diabatic P potential in polar acetonitrile affects the S_1/S_0 crossing (pyramidalized) that approaches the stationary point within P (nonpyramidalized), resulting in the barrier lowering.

Next, compound t4 represents the smallest homologue in the series of bridged stilbene derivatives. Due to an increase in the S₁ torsional barrier of ~2–3 kJ/mol (Table 1), the progression to P is delayed by a factor of 2–3 in *n*-hexane ($\tau_i = 166$ ps) and acetonitrile ($\tau_i = 114$ ps). The increase in E_b can be ascribed to the reduced steric interactions compared to t0, where the repulsion between phenyl and ethylenic hydrogens disfavors the planar trans configuration.



Figure 7. Evolution kinetics of t6 in *n*-hexane (left) and acetonitrile (right). Top panels show that an ultrafast $S_1 \rightarrow P$ transition is recognized by S_1 decay (blue) and P development (red). Red-shifted SE is seen as a negative signal about t = 0.2 ps. The $P \rightarrow S_0$ decay is shown at the bottom, with $\tau_p = 1840$ ps in *n*-hexane and 35 ps in acetonitrile.

Table 3. Lifetime τ_P of Perpendicular State P and P \rightarrow S₀ Barrier E_{b2} in Stilbenes

pump-probe delay t (ps)

	t0		€ ∕Q	Ŝ∕o	÷.	
n-hexane	0.3 ps ⁴ 2.7 kJ/mol	27 ps ⁸ 14 kJ/mol	19 ps ⁷ 13 kJ/mol	45 ps ⁷ 15 kJ/mol	-	1840 ps 24 kJ/mol
acetonitrile	0.4 ps ⁴ 3.4 kJ/mol	2.1 ps ⁸ 7.4 kJ/mol	2.9 ps ⁷ 8.2 kJ/mol	3.4 ps ⁷ 8.6 kJ/mol	134 ps ⁸ 18 kJ/mol	35 ps 14 kJ/mol

Switching to trans stiff t5 with two bridging methylene units,¹⁰ here, more flexible five-membered rings sterically interact with the opposite phenyl rings, giving rise to a broader extinction spectrum. The steric effects reduce the $S_1 \rightarrow P$ torsional barrier to $E_b = 10$ kJ/mol in *n*-hexane and 7 kJ/mol in acetonitrile (Table 1), and the photoisomerization time τ_i decreases to 5 and 2 ps, respectively.

The last representative t6 further follows this trend. In both solvents, torsion to P proceeds without a barrier, reflecting the planar conformation to be highly unstable in S_1 . The very proximity of the phenyl rings to the *tert*-butylene units causes strong steric repulsion, yielding a broad distribution of adopted dihedral angles distinct from 180° (planarity). This large structural variety is reflected in a broadened extinction spectrum, which also involves an amplitude drop down. As the twisted configuration must already be largely attained in S_0 , torsion in S_1 should proceed very fast, and the formation of P becomes visible in the transient spectra. The corresponding ESA band is identified by comparing to other stilbenes.^{4,6–8}

The ring size, likewise, affects the stability of the excited cis conformation. In the almost planar excited c4, where the



pump-probe delay t (ps)

Figure 8. Diabatic energy surfaces to understand the experimental results. For t4 (top), the $S_1 \rightarrow P$ barrier E_{b1} is relatively high lowers in acetonitrile compared to *n*-hexane, while the $P \rightarrow S_0$ barrier E_{b2} is small enough to assure the same bleach recovery time as the $S_1 \rightarrow P$ time τ_i . On the contrary, for t6 (bottom), the $S_1 \rightarrow P$ barrier E_{b1} is negligible, whereas the $P \rightarrow S_0$ barrier E_{b2} is substantial and depends on solvent polarity (lowers in acetonitrile relative to *n*-hexane).

opposite phenyl rings interact only marginally, the torsional lifetimes ($\tau_i = 64$ ps in *n*-hexane and 45 ps in acetonitrile) are comparable to those of t4 ($\tau_i = 166$ ps in *n*-hexane and 114 ps in acetonitrile). Another consequence of the structural rigidity

and planarity is that the S_0 and S_1 absorption spectra of c4 and t4 become similar in shape. However, due to a slight spectral shift between both (~1 nm), addition of a reasonable amount of ε_{t4} to the late TA bleach eventually produces the c4 extinction spectrum. Unfortunately, the accuracy of this approach reduces with increasing spectral resemblance of the isomers. The E/Z ratio in S_0 calculated with S_1 spectra gives 1:1 in both acetonitrile and *n*-hexane, in good agreement with the NMR results (1:1). In less planar c5, the $S_1 \rightarrow P$ barrier lowers (see Table 2), and in t6, no stable cis isomer is produced at room temperature in S_0 .

The computational results of the present and previous works suggest an explanation for the trends in the lifetime of the P state. It turns out that the S_1/S_0 minimum energy crossing point, through which the relaxation to S₀ proceeds, is always highly pyramidalized, so that the S₀ potential energy surface steeply approaches S₁ along the pyramidalization coordinate. The stationary point of the P state in S₁ also shows a clear tendency to pyramidalize, but it may be counterbalanced by the steric strains brought about by the narrowing valence angles at the pyramidalized site. Those strains become more severe when the substituents are bulkier. In that case, the stationary point should be less pyramidalized and thus farther in terms of both energy and geometric changes from the barrier at the S_1/S_0 crossing point. Indeed, the four-membered ring in 4 keeps one of the valence angles below 90°, thus providing more room for pyramidalization through narrowing of the two other valence angles (see Figure 5). On the contrary, in 6, the valence angles in the six-membered stiffening rings remain at ~115-120°, effectively preventing the pyramidalization, even though the charge separation in the molecule is as strong as in other stilbenes. Furthermore, as seen from Table 3, simple alkyl substituents in nonstiffened compounds deliver the same effect, and the P lifetime directly correlates with their size. Thus, substitution at the ethylenic sites provides convenient means for controlling the P lifetime. However, at the same time, bulkier substituents likely reduce the S₁ lifetime through steric interaction. To decouple the two effects, one may try a combination of ethylenic and ring substitution that can alter the electronic structure of the trans and cis domains in S_1 and effectively increase the lifetime.⁹

5. CONCLUSIONS

Substitution plays an important role in the evolution of stilbenes. We have recently demonstrated⁹ that the phenyl ring substitution results in alteration of the electronic structure of S₁ in the vicinity of the Franck–Condon geometries. The present data help one to rationalize the effects of substitution at the central ethylenic sites. Comparison of stiffened stilbenes t4, c4, and t6 with previously studied parent stilbene t0 and c0, stiff stilbenes t5 and c5, and several other substituted stilbenes reveals a dual steric effect of both the stiffening rings and monovalent substituents. On the one hand, bulkier groups and larger stiffening rings destabilize the excited trans and cis conformation due to stronger steric repulsions between the halves of the molecule and thus reduce its lifetime. On the other hand, they hamper pyramidalization of the ethylenic centers in the P state, which is a necessary prerequisite for reaching the ground state through the S_1/S_0 crossing and hence increases the P lifetime. Those details of the P-state behavior also affect the trans-to-cis photoisomerization yield that requires a separate study. Thus, by combining various

substitution motifs in stilbenes, one can tune the photochemical behavior.

A rather technical aspect is addressed by the estimate of the S_0 population ratio of co-excited t4 and c4. Due to the structural rigidity and planarity, their extinction spectra share very similar shapes but are not identical. Conveniently, it follows that the S_0-S_1 spectrum of c4 can be reconstructed with the help of late TA spectra. Accordingly, upon excitation, both isomers have their S_1 states populated with known probabilities, and the bleach bands of the corresponding species reflect their S_0 population. Alternatively, for purely measured t4, the separation of trans from cis follows from their distinct isomerization rate to P, with cis being accelerated by a factor of 2 to 3. A global kinetic analysis allows to discern the characteristic TA traces and to catch the corresponding species-associated spectra.

Very interesting results are obtained for t6. First, the $S_1 \rightarrow P$ torsion here is fully barrier-less, similar to stilbenes with olefinic substitutions.^{6–8} Second, the P state is very long-lived, 1840 ps in *n*-hexane, which is currently the longest lifetime of the perpendicular state in stilbenes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.9b00784.

Additional data on the results from stationary and transient absorption, NMR measurements determining the relative mole fractions of t4 and c4 in the mixtures, and optimized coordinates for geometries from quantum chemical calculations (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: quickmaq@chemie.hu-berlin.de (M.Q.). *E-mail: ioffe@phys.chem.msu.ru (I.N.I.).

ORCID 💿

Martin Quick: 0000-0002-9029-8802

Sergey A. Kovalenko: 0000-0003-4278-9305

Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to the memory of "Doc" Leo A. Paquette (1934–2019).^{31,32}

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