Torsional Photoisomerization Proceeding Adiabatically Through a Volume-Conserving Pathway in Uninhibited Fluid Media

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Although the photochemical *cis–trans* isomerization pathways of organic molecules and biomolecules have been studied for a long time, mechanistically these reactions remain to be fully understood.[1] It is generally accepted that photochemical isomerization processes in uninhibited fluid media usually involve large-amplitude motion (torsional relaxation) of a bulky group twisting around a molecular axis (one-bond-flip OBF). In contrast, efforts targeted to satisfactorily explaining diabatic photoisomerization of organic molecules sterically hindered in volume-restricted media, such as organic glass, crystals, cavitands, and proteins, have led to the establishment of two discrete volume-conserving photochemical mechanisms; the bicycle-pedal[2] (BP) and the hula-twist[3] (HT) mechanism. These involve conformational rearrangements proceeding, upon excitation, by small-amplitude torsional flexibility; that is, concerted rotation about more than one bond in a manner to minimize volume requirements. Warshel's bicycle-pedal mechanism[2] (BP) involves simultaneous rotations of two *alternating* double bonds, while the other fragments of the molecule remain in plane. In a hula-twist (HT) mechanism,[3] a pair of *adjacent* double and single bonds rotates concertedly leading to an out-of-plane inversion of a C−H unit (for polyenes); meanwhile, the other parts reorient within the plane. Although the above mechanisms were initially postulated to explain medium-directed photoisomerization of olefins and polyenes, the recent literature suggests the involvement of heteroatomic quasi-single bonds, such as C$\doteq$N (photochromic salicylideneaniline)[4] and C$\doteq$S (thiocinnamate chromophore of PYP),[4] in analogous processes. A somewhat different concerted two-bond twist process has also been proposed to explain the diabatic volume-saving *syn–anti* photoisomerization for chromophores bearing lone-pair electrons (n→π* transitions) such as azomethines (R^{1}R^{2}C=N−H) and the related azobenzenes[1b]. For these compounds the photoisomerization is driven possibly by an in-plane inversion process (pyramidal inversion process of a C=N or an N=N bond) centered at one nitrogen atom.

The implication of one-photon two-bond isomerization in the above mechanisms, has led the community[3d,5] to suggest that the key step of the photoisomerization reaction is a radiationless transition between the S_1 and S_0 states; that is, the initially formed Franck-Condon excited conformer lowers its energy across the S_1 potential surface through twisting one double bond until it reaches the perpendicular structure, which is subsequently funneled through the S_1/S_0 conical intersection (CI) to the ground surface, at which the concerted motion is completed. Concerted rotation about two bonds in the ground state (thermally) has been commonly observed in condensed-phase media for a variety of compounds, including artificial molecular rotors in unhindered environments,[6] conformationally flexible polymers,[7] organic chromophors,[8] biomolecules,[9] and so forth.

Nevertheless, to the best of our knowledge, there is no evidence on whether concerted rotation about two bonds could drive an isomerization on a purely adiabatic excited surface. It is generally believed that for adiabatic *cis–trans* photoisomerization reactions—in which the CI evidently is not present—the one-photon one-bond isomerization OBF mechanism is the dominant pathway regardless of the nature of the medium.

Previously it has been shown that 2-methoxynaphthalene (**1**) can exist in the gas and liquid phase in two different spectrally distinct conformations *cis* (*syn*) and *trans* (*anti*), which may interconvert torsionally (around the $C_{aryl}\doteq O$ "double" bond by 180°) both thermally[10] and photochemically[11] (Scheme 1). Similar observations were made recently for 2-methoxyanthracene and some of its derivatives in solution.[12]

Herein we present results on the excited-state kinetics and thermodynamics of adiabatic conformational interconversion in centrosymmetrically disubstituted naphthalenes
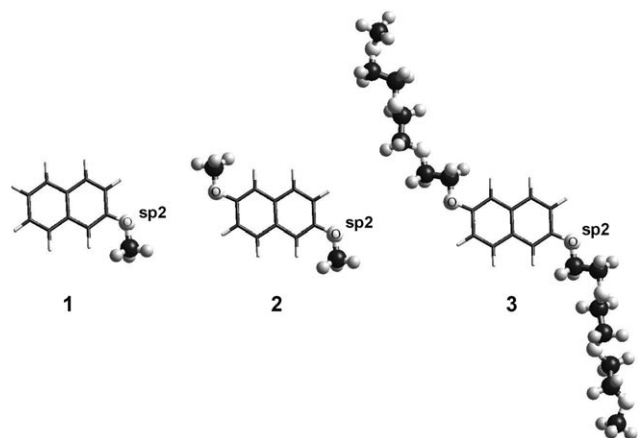
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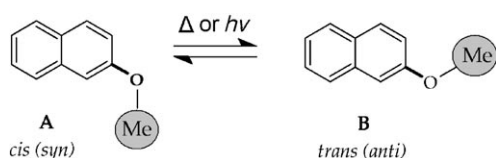
Scheme 1. Rotational isomers of **1**; the *cis* (*syn*, $\phi \approx 0°$) and *trans* (*anti*, $\phi \approx 180°$) configurations are denoted by the dihedral angle ϕ formed by the naphthalene plane and the O−Me bond vector.

when dissolved in 3-methylpentane (3-MP) and in the more viscous hydrocarbon tetradecane (C_{14}). The tested compounds **2** and **3** were synthetically designed to differ significantly in exocyclic bulkiness, namely 2,6-dimethoxynaphthalene (**2**) and its analogue (**3**) in which each methoxy group of **2** is replaced with the bulky but photochemically inert methoxytriethylene glycol moiety. If it is true that adiabati-

cally interconvertible rotational isomers in S_1 only follow the OBF isomerization mechanism, then one would expect that the exocyclic bulkiness and the viscosity of the medium would dramatically affect the rate following the movement of the twisting bulky group and accordingly the S_1 thermochemistry.

X-ray crystallography[13] proves that the almost planar *cis* configuration of **1** is the energetically favorable form in the ground state. Similarly, the crystal structure[14] of **3** (Figure 1) shows that it crystallizes as a nearly planar mole-
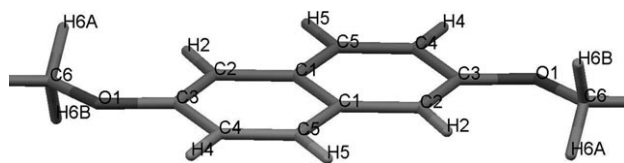

Figure 1. Partially labeled plot of the *cis,cis* form of **3** in the crystal state.[12] Selected bond distances of the aromatic subunit: C1−C2 = 1.419; C2−C3 = 1.373; C3−C4 = 1.417; C4−C5 = 1.357; C5−C1 = 1.418; C1−C1 = 1.418 Å. Selected exocyclic bonds: C3−O1 = 1.366, O1−C6 = 1.426°. Torsional angle ϕ(C2-C3-O1-C6) = 6.7°; angle ϕ(C3-O1-C6) = 118.3°

cule with each −OG (G: $C_7H_{15}O_3$) group adopting a synperiplanar (*cis*) conformation (dihedral ϕ(C2-C3-O1-C6) = 6.7°). Yet, the angle ϕ(C3-O1-C6) = 118.3° nearly matches the unperturbed one (120.0°) of a perfectly sp²-hybridized atom, suggesting significant resonance interactions between the naphthalene's orbitals and the oxygen's lone electron pair lying perpendicularly to the aromatic plane. Accordingly, the exocyclic C3−O1 link appears to be essentially a double bond with a length (1.366 Å) significantly shorter than a typical single C−O bond length (1.43 Å in methyl ether[15]).

Quantum mechanical calculations at the RHF[16] and DFT[14] level of theory also support the conformational preference of the *cis* isomer of the reference compound **1**. Furthermore, both methods predict an additional local energy minimum in S_0 with a methoxy torsional angle of $\phi \approx 180°$ (planar *trans* rotamer). It lies ≈ 5.9 kJ mol⁻¹ (DFT) higher in energy than that of the *cis* analogue and the barrier to rotation of the methoxy group was calculated to be ≈ 10 kJ mol⁻¹.[16] The simultaneous existence of the above rotational isomers of **1** and the *cis* conformational preference has also been confirmed experimentally in the gasphase[10a] and in solution.[10b,c, 11] An enhanced stability of ≈ 6.5 kJ mol⁻¹ of the *cis* configuration in S_0 was found in 3-methylpentane[11] in agreement with the DFT calculations. Furthermore, we have unambiguously demonstrated that in S_1 the two rotamers of **1** are nearly isoenergetic and equilibrate adiabatically above 260 K through an almost fully reversible isomerization path and an activation barrier[11] of 29 kJ mol⁻¹.

The photodynamic scheme under discussion is shown in Scheme 2.
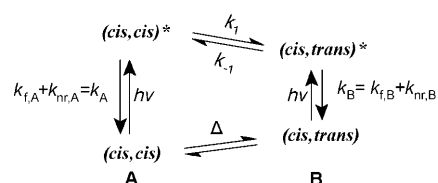
Scheme 2. Photodynamic scheme for the isomerization of the compounds under investigation (**2** and **3**); k_1 and k_{-1} are the forward and reverse excited-state isomerization rate constants, respectively. The non-isomerization rate constants k_A and k_B are expressed as the sum of the radiative and nonradiative rate constant of the corresponding excited species.

Figure 2 displays the temperature dependence of the absorption spectrum of **2** dissolved in 3-MP, upon cooling stepwise from 296 to 77 K. The gradual disappearance of the shoulder at the red edge of the spectrum and the presence of several isosbestic points across the absorption spectrum strongly suggest the simultaneous existence in the ground-state of two discrete forms in thermal equilibrium; namely the predominant thermodynamically stable *cis,cis* (**A**) and the energetically closest lying *cis,trans* (**B**) form in agreement with theoretical predictions.[14] Their electronic π–π* origin transitions S_1–S_0 separate by ~580 cm⁻¹ nearly matching that of *cis* and *trans* rotamers[11] of **1** (≈ 630 cm⁻¹). We
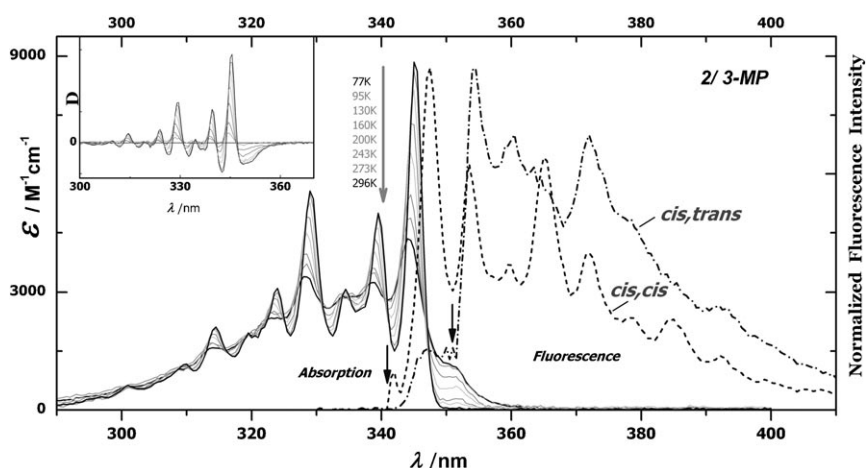
Figure 2. Absorption spectra of **2** in 3-MP (4.8×10^{-5} M) at varying temperatures corrected for temperature dependence of the density of the solution; Insert left top: Difference spectra (296-T) Right: pure emission spectra of *cis,cis* and *cis,trans* rotamers obtained respectively at 77 and 160 K (see arrows for excitation).

note also that the absorption spectrum at 77 K closely resembles that of crystals in which the **A** conformer was solely observed by X-ray analysis.[14]

Below 260 K the S_1 thermally activated interconversion rate $k_1 + k_{-1}$ is suppressed, thereby permitting a purely photoselected rotameric analysis to be made. The results demonstrate that the above conformers **A** and **B** have nearly indistinguishable quantum yields ($\Phi = 0.38 \pm 0.03$) and lifetimes ($\tau_{0,A} = \tau_{0,B} = 8.6 \pm 0.2$ ns). It is also worth noting the independence of Φ on temperature and excitation wavelength over the wide temperature region studied (77 to 342 K), suggesting further the absence of a thermally activated nonradiative decay channel (for an extensive and comprehensive analysis see the Supporting Information section I). We note also that the photochemically inert bulky moieties of **3** do not affect the photophysical properties of the aromatic core differently than the methoxy groups of the precursory compound **2**.[14]

Above 260 K a pure adiabatic interconversion channel in the π–π* singlet excited state between **A*** and **B*** rotamers is switched on, as manifested by both dynamic and static fluorescence spectroscopy. We observe coupled biexponential kinetics with short (τ_1) and long (τ_2) lifetime components, showing no wavelength dependence. Upon analyzing the decay traces at emission wavelengths at which **B*** predominantly emits, for example, 400 nm, the sign of the preexponential factor of the τ_1 becomes negative, suggesting that **A*** is the kinetic precursor to the rising component **B***. It can be shown that if $k_A \approx k_B$ (Scheme 2) then the isomerization $k_1 + k_{-1}$ and nonisomerization rate constants k_A and k_B can be related straightforwardly with the recovered lifetimes [Eqns. (1) and (2)].[17] (For a rigorous analysis see the Supporting Information section II).

$$\tau_1^{-1} - \tau_2^{-1} = k_1 + k_{-1} = k_{sum} \tag{1}$$

$$\tau_2^{-1} = k_B \approx k_A \tag{2}$$

When decay traces are detected in a narrow wavelength region owing to the emission of the **A*** isomer only, for example, $\approx 345 \pm 2$ nm, then we obtain the following Equation (3) from which the forward isomerization rate constant k_1 can be evaluated (error $\approx 10\%$):

$$k_1 = [1/(1+\alpha) + K_{eq}^{S_0}](1 + K_{eq}^{S_0})^{-1}(\tau_1^{-1} - \tau_2^{-1}) \tag{3}$$

In Equation (3) $\alpha = \alpha_2/\alpha_1$ is the quotient of the preexponential factors of the fitting function and $K_{eq}^{S_0}$ is the equilibrium constant of the thermal isomerization in S_0, which is estimated roughly to be ≈ 0.20–0.25 at 296 K, regardless of solvent and exocyclic substitution.

The temperature dependence of the recovered rate constants when compounds **2** and **3** are dissolved in 3-MP and C_{14}, are shown in Figure 3. It is clearly seen that the forward (k_1) and reverse (k_{-1}) excited-state isomerization rate constants are almost completely independent of exocyclic bulkiness and medium viscosity.

It follows that the above factors do not influence distinctly the S_1 thermal activation parameters evaluated by an Arrhenius analysis [Eq. (4)]

$$k_1 + k_{-1} = k_{sum} = k_1^0 \exp(-E_a^1/RT) + k_{-1}^0 \exp(-E_a^{-1}/RT) \tag{4}$$

1) The magnitude of the potential energy barrier (interconversion; $E_a^{sum} = 24$ kJ mol^{-1}, forward; $E_a^1 = 22$ kJ mol^{-1} and reverse; $E_a^{-1} = 32$ kJ mol^{-1}).
2) The reaction enthalpy $-\Delta H^{S1} = E_a^{-1} - E_a^1 \approx 10$ kJ mol^{-1} and entropy $\Delta S^{S1} = R\ln(k_1^0/k_{-1}^0) \approx -15$ J K^{-1} mol^{-1}.
3) the free energy of isomerization $\Delta G_{298 K}^{S_1} \approx -5$ kJ mol$^{-1} = -RT\ln K_{eq}^{S_1}$. That is, the excited-state rotameric equilibrium $K_{eq}^{S_1}$ is not affected at all.

These experimental manifestations conclusively demonstrate that the shape of the potential-energy surface by the reaction *cis,cis* → cis,trans** persists intact upon the influence of increased solvent viscosity and exocyclic bulkiness of the tested compounds (see the Supporting Information section III). The absence of a measurable effect of these factors on $K_{eq}^{S_1}$ can also be determined indirectly from the photostationary spectra at 296 K. The $K_{eq}^{S_1}$ can be expressed by the fractional quantum yields quotient [Eq. (5)].[11]

$$K_{eq}^{S_1} \cong [B^*]/[A^*] \cong \Phi_B/\Phi_A \tag{5}$$

The area of the **B*** spectrum was retrieved by subtracting from the total emission spectrum the fraction of the **A***
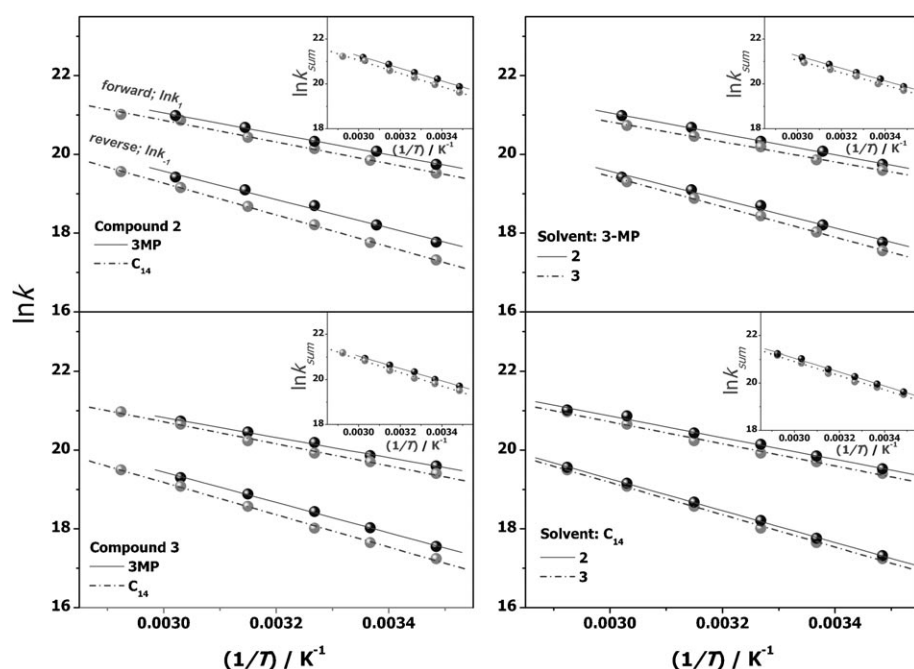
Figure 3. Combination charts of Arrhenius plots for the forward k_1 and reverse k_{-1} isomerization rate constants of compounds **2** and **3** dissolved in 3-MP and C$_{14}$. Inserts: Arrhenius plots for the interconversion isomerization process $k_{sum} = k_1 + k_{-1}$ obtained directly from the fitting equation to the fluorescence decay traces.

spectrum, according to the pure rotameric spectral analysis made before at low temperatures. The insensitivity of $K_{eq}^{S_1}$ to exocyclic bulkiness is clearly illustrated in Figure 4 (insert). After analysis we obtain an estimation of $K_{eq}^{S_1} \approx 4.5$–5.0, which is in reasonable agreement with that obtained by dynamic fluorescence kinetic analysis ($K_{eq}^{S_1} \cong k_1/k_{-1} \approx 6.5$).

We obtain a third estimation of the magnitude of $K_{eq}^{S_1}$ by comparing the early- and late-gated time-resolved emission
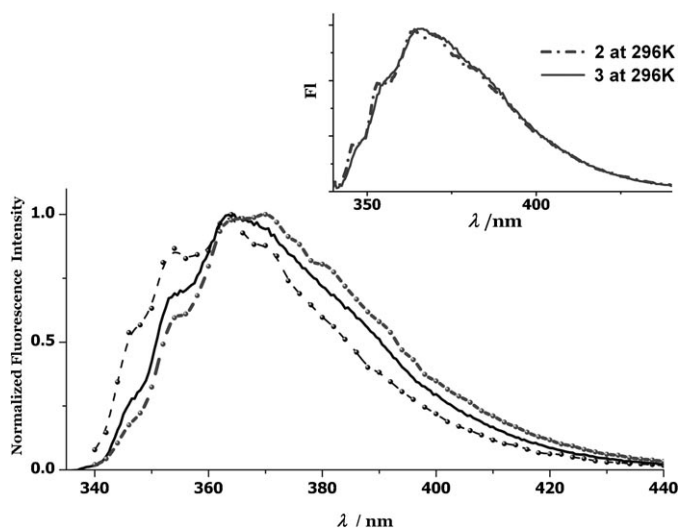

Figure 4. Normalized early- (-----) and late- (–•–•) gated time-resolved emission spectrum of **2** in 3-MP, observed respectively at ∼500 ps and 5 ns after excitation; the solid line is the photostationary fluorescence spectrum. Insert: Photostationary fluorescence spectra of **2** and **3** in 3-MP at 296 K.

spectrum to the photostationary emission spectrum at ≈296 K. At short times after pulse excitation the early-gated emission spectrum (dash line) is composed predominantly of the unequilibrating mixture of **A*** and **B*** rotamers. In the late-gated spectrum (dash-dot line, delay ≥5 ns) dynamic equilibrium is fully established in S$_1$. This means that the relaxed time-resolved emission spectrum closely resembles the time-integrated (photostationary) spectrum (solid line) at room temperature. Following the procedure described above the estimation for $K_{eq}^{S_1}$ leads roughly to a value of ≈6.0–6.5. Similar results were obtained for all cases.

By means of Kramer's theory[18] an isomerization rate constant k_{iso} can be approximately expressed[17] [Eq. (6)] in terms of the intrinsic transition-state rate constant k^{tst} and the transmission coefficient κ, which corrects the tst rate constant for non-tst effects, such as recrossing of the top of the potential barrier as a result of collisions with solvent molecules (see the Supporting Information section IV)

$$k_{iso} = \kappa k^{tst} \tag{6}$$

Briefly, κ is a function mainly of the reduced moment of inertia of the moving group and of the friction exerted by the solvent molecules on it. Scaling shape factors of the moving group and boundary conditions between solute–solvent were also considered strictly in our estimates[1a]. If the *cis,cis*→*cis,trans** adiabatic photoisomerization was to occur through a movement of the bulky group along the surface of a cone (torsional relaxation around the C$_{aryl}$═O "double" bond) strong hydrodynamic friction, at least for **3**, would be present (Figure 5).

Surprisingly, this prediction is almost completely inconsistent with our experimental observations in which we clearly demonstrated the absence of a measurable solvent and exocyclic substitution effect on the S$_1$ thermochemistry. The findings conclusively imply that the present adiabatic photoisomerization proceeds by a volume-saving mechanism that locally inverts the sp^2-hybridized oxygen atom, leaving the other molecular fragments nearly static (at least for **3**). This kind of local motion should definitely involve the in-plane or the out-of-plane inversion of the planarized oxygen atom linked to the aromatic subunit (Scheme 3).

It is believed that the in-plane inversion accounts for the *syn–anti* diabatic isomerization of azomethines (R^{1}R^{2}C=N–
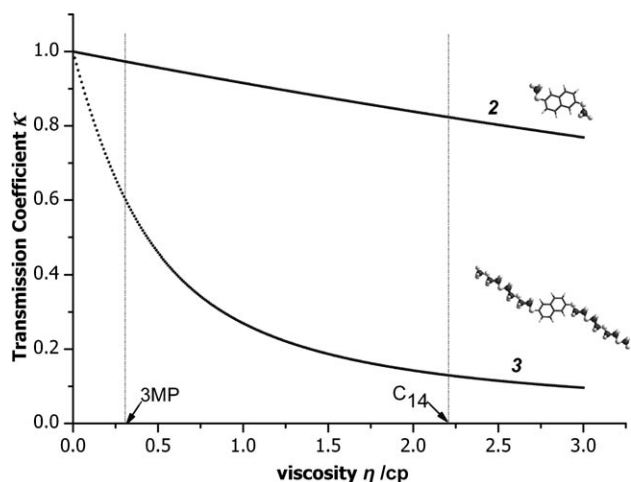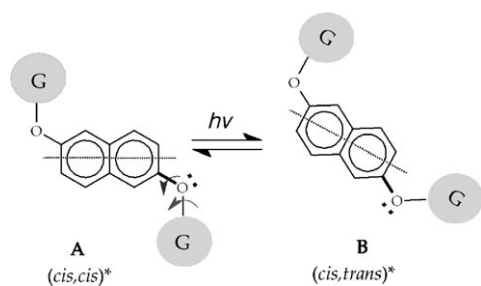
Figure 5. Simulated curves of the transmission coefficient κ versus viscosity η obtained for a hypothetical torsional relaxation of the bulky group around the C_{aryl}=O "double" bond.

Scheme 3. Out-of-plane inversion of the sp^2-hybridized oxygen atom (hula-twist) leading to the interconversion between cis,cis* and cis,trans* conformers

H) and the related azobenzenes[1b] and is dominated by $n \rightarrow \pi*$ transitions, although recent high-level computational studies do not support this mechanism.[19] Moreover, we did not observe an $n \rightarrow \pi*$ transition here. In other words our findings strongly suggest that a local ~180° out-of-plane inversion of the oxygen atom, closely resembling the HT concept, most likely takes place. It is interesting to note the suggestion recently addressed by Fuss et al.[20] that HT mechanism might reveal itself through the S_1/S_0 conical intersection, at least for nonpolar polyenes, in all photoisomerization reactions, including those in solution at room temperature.

In conclusion our results clearly demonstrate by straightforward kinetic analysis that two distinct cis,cis* and cis,-trans* conformations interconvert during their lifetime (≈ 10 ns) in S_1. This suggests that the sp^2-hybridized oxygen atom should be effectively inverted adiabatically between the equilibrium geometries of two periplanar configurations (syn, $\phi \approx 0°$ and anti, $\phi \approx 180°$). In other words, a photo-

chemically stimulated simultaneous rotation of two adjacent bonds (a double and a single one) may be possible in a pure potential-energy surface of the excited singlet state in solution. This differs radically from what is generally accepted for volume-saving photochemical cis–trans isomerization pathways of organic chromophores, for which the key step is the motion through the funnel (S_1/S_0 intersection), leading to the decay to S_0 and to completion (thermally) of the isomerization.

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