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The Anomalous Excited-State Temperature Behavior of *trans*-4,4′-Diaminostilbene and *trans*-4,4′-Di(phenyl-ureanyl)-stilbene

Matthias Seydack and Jürgen Bendig*

Institute of Chemistry, Humboldt University, Hessische Strasse 1-2, 10115 Berlin, Germany

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Photoisomerization of *trans*-stilbene and its derivatives is known to proceed via an activation step from the S_1 (and in some cases also T_1) state. Accordingly, the activation energy of this process can in principle be determined either by measuring the quantum yields of isomerization directly or by analyzing the temperature behavior of the fluorescence quantum yield (Arrhenius plot) instead. Since both techniques are expected to produce the same result, many authors prefer the latter because of easier feasibility. In this letter, we show that at least for some donor substituted *trans*-stilbenes, this is not justified: parallel measurements of fluorescence and isomerization quantum yields of *trans*-4,4′-diaminostilbene and *trans*-4,4′-di(phenyl-ureanyl)-stilbene as a function of temperature exhibited a decrease of the quantum yields of fluorescence and isomerization with increasing temperature. We deduce the presence of a second activated process, responsible for reducing ϕ_f and $\phi_{t\to c}$ and for governing the anomalous temperature dependence of $\phi_{t\to c}$.

Introduction

Over the past decades, stilbene isomerization has turned out to be a rather complex mechanism, depending on diverse internal and external factors such as solvent polarity and viscosity, sensitizers, concentration, irradiation wavelengths, electron pulling/pushing groups, heavy atoms, and the introduction of deuterium and steric hindrance.[1] In the generally accepted model,[2,3] the process of isomerization proceeds from the excited S_1 state $^1t^*$ (with nitro- and heavy atom substituted stilbenes[4] also from the triplet state $^3t^*$) via an activation barrier to a pericyclic minimum state $^1p^*$, which is known to arise from a mixing of the S_1 state with states of doubly excited configurations and is often identified with a conical intersection (Figure 2).[5] It is represented by a perpendicular geometry. From $^1p^*$, a relaxation to either the trans or the cis ground state (^1t and ^1c) is equally probable; i.e., the partition ratio is 0.5.

Donor−donor substitutuents in p,p′ positions are known to participate in the excited-state electron delocalization and thereby stabilize the $^1t^*$ state; i.e., the activation barrier will be higher than that of unsubstituted stilbene. Because of this fact, the rates of isomerization are reduced. From this point of view, *trans*-4,4′-diaminostilbene (DAS) and *trans*-4,4′-di(phenyl-ureanyl)-stilbene (DPS, Figure 1), a model compound mimicking a subsystem in some triple chromophoric molecules,[6] could be expected to behave photochemically similarly. To check up on this, we measured temperature-dependent quantum yields of fluorescence and isomerization. The results are compared to activation energies, and quantum chemical ab initio DFT calculations were performed to ascertain the ground-state dipole moment of DPS.

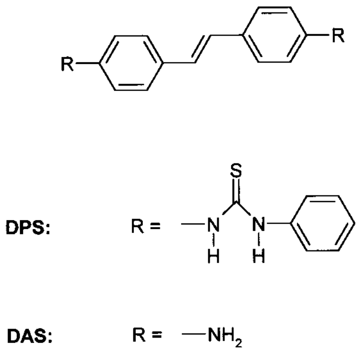

Figure 1.

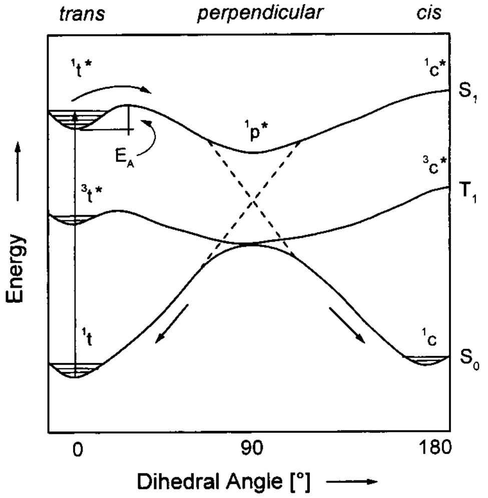

Figure 2. Schematic representation of the potential energy curves (projection of a multidimensional reaction space into the hypersurface of the dihedral angle) for stilbenes and the fate of the ground-state trans isomer after optical excitation.

Results and Discussion

DPS was found to exhibit a deactivation behavior that was quantitatively very different from that of *trans*-stilbene but also from that of DAS. The quantum yields of isomerization and fluorescence were unexpectedly small (all data in MeOH):

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* Corresponding author. E-mail: juergen=bendig@chemie.hu-berlin.de.

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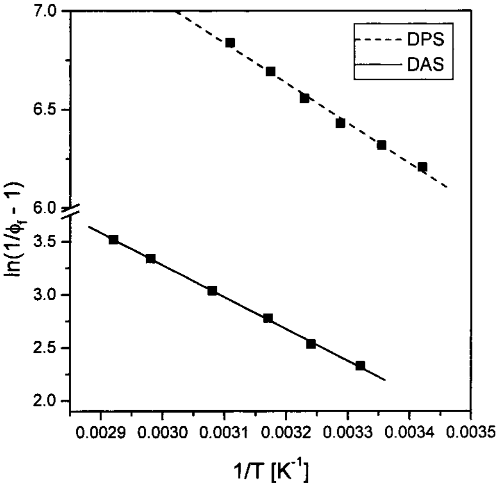

Figure 3. Arrhenius plot of DPS/DAS fluorescence in MeOH, assuming a model with one temperature-dependent deactivation step.

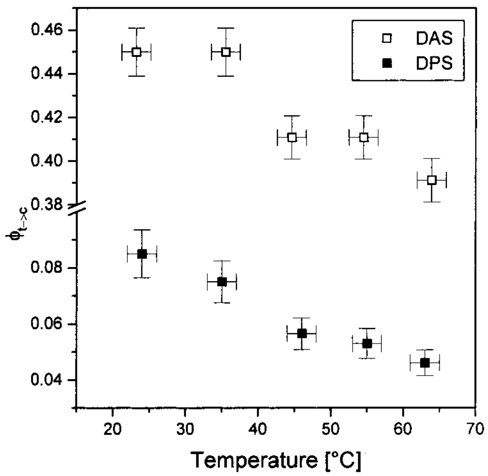

Figure 4. Quantum yield of the trans → cis isomerization of DPS and DAS in MeOH vs temperature.

$\phi_{t\rightarrow c} = 0.085$, and $\phi_f = 0.0018$ (DAS, $\phi_{t\rightarrow c} = 0.45$ and $\phi_f = 0.10$, which is in good agreement with literature data;[1,7] cf. *trans*-stilbene[1], $\phi_{t\rightarrow c} = 0.48$ and $\phi_f = 0.04$). On the other hand, there was no indication of a populated triplet state for DPS and DAS: at 77 K, no phosphorescence could be detected (neither in MeOH nor in EPA, nor could it be induced by an external heavy-atom effect in 1:9 mixtures of MeOH:CHBr$_3$). Sensitizing experiments with methylene blue, rose bengal, fluorescein, 2,3,5,6-tetramethyl-1,4-benzoquinone, and perylene at room temperature afforded no *cis*-DPS isomer. This indicates that the triplet state $^3t^*$ plays no vital role in the deactivation pattern of DAS and DPS and cannot be held responsible for their fluorescence and isomerization behavior. At this point, it seemed reasonable to investigate the activation energy of DPS and DAS in the $^1t^*$, state as a very high barrier could at least account for the minute quantum yields of isomerization. First, the quantum yields of fluorescence ϕ_f were measured in their dependence on temperature. Taking the isomerization as the only temperature-dependent deactivation channel, one arrives at eq 1 for the relationship between ϕ_f and the activation energy E_A

$$\ln\left(\frac{1}{\phi_f} - 1\right) = \ln\frac{k_{iso}}{k_f} - \frac{E_A}{RT} \qquad (1)$$

Here k_{iso} and k_f denote the rates of isomerization and fluorescence. This equation holds for the case that $\phi_f = 1.0$ at $T = 0$ K. Plotting $\ln(1/\phi_f - 1)$ versus $1/T$ affords the activation energy E_A (Figure 3). We obtained a value of $E_A = 16 \pm 2$ kJ/mol for DPS and $E_A = 23 \pm 2$ kJ/mol for DAS. The latter value is close to data from literature[7] for DAS in EtOH, while the former compound was measured for the first time. In other solvents, however, the Arrhenius plots were clearly nonlinear. For clarification, the quantum yields of isomerization were now measured directly as a function of temperature. According to the model (Figure 2), $\phi_{t\rightarrow c}$ is expected to increase with increasing temperature because higher vibronic sublevels of the $^1t^*$ state are more efficiently populated, making it easier to surmount the activation barrier. (Viscosity effects could be excluded by determining viscosity related activation energies of the solvents by means of Andrade plots and following the argumentation given by Smit and Ghiggino[8]). The experiments, however, produced the opposite result: $\phi_{t\rightarrow c}$ decreases as the temperature is increased (Figure 4). This effect is much more conspicuous with DPS than with DAS.

Applying an equation by Strickler and Berg[9] in combination with the quantum yields of fluorescence, one obtains fluorescence lifetimes of $\tau_f = 2.1$ and 189 ps for DPS and DAS, respectively. While the value for DAS is consistent with the results obtained by other authors for substituted *trans*-stilbenes in polar, low-viscosity solvents (typically 30−560 ps[7,8,10,11]), the value for DPS is more than 1 order of magnitude smaller.

These experimental results clearly indicate the existence of a further deactivation process for singlet excited DPS and DAS, competing with fluorescence and isomerization. Going from highly polar MeOH to less polar solvents like tetrahydrofuran (THF), the temperature dependence of $\phi_{t\rightarrow c}$ became less marked, which means that this competing process becomes less effective in media of reduced polarity. By analogy with the polarity dependence of molecules populating TICT states as an additional deactivation channel,[12,13] we draw the conclusion that an efficient nonradiative channel exists for DPS and DAS, which is connected with a reduction of symmetry. This nonradiative channel may be induced by a twisting process around one or more single bonds. In aggreement with a number of well-studied TICT compounds[14,15] but in contrast to a recent study of 4-aminostilbenes,[16] such twisted excited-state conformations of DAS and DPS would have to be nonfluorescent. Only moderately dependent on solvent polarity, the Stokes's shift for DPS varies from only 4000 to 5150 cm^{-1}. Since the ground-state dipole moment was calculated to be $\mu_g = 4.86$ D and the solvatochromic slopes of absorption and fluorescence maxima are of comparable magnitude, this is clear evidence that the emission of DPS does not originate from a TICT state but from a locally excited (LE) state.

For the overall quantum yield of all nonradiative processes for both isomers taken together, we obtain values of $\phi_{nr}^{t} + \phi_{nr}^{c} = 1.63$ and 0.38 for DPS and DAS respectively (see Supporting Information). Therefore, this "new" process is the dominant relaxation channel for excited DPS. In DAS, its influence on the deactivation is much smaller but far from negligible.

An alternative interpretation is the assumption of a "nonclassical" isomerization behavior with a temperature-dependent partition ratio from $^1p^*$. Then the rate constant leading back to the trans isomer could be enhanced with temperature relative to the forward rate constant. In this case, the sum of $\phi_{t\rightarrow c}$ and $\phi_{c\rightarrow t}$ may exceed 1.0. This, however, was not observed (Table 1). A direct way to discriminate between both models is to compare our data with those of bridged model compounds. We hope to present such data in the near future.

TABLE 1: Comparison of Selected Deactivation Quantum Yields[a]

	trans-stilbene	DAS	DPS
ϕ_f	0.04[b]	0.10	0.0018
$\phi_{t\rightarrow c}$	0.48[b]	0.45	0.085
$\phi_{c\rightarrow t}$	0.32[b]	0.41	0.102

[a] Experimental error for DAS and DPS: $\phi_{t\rightarrow c}$ and $\phi_{c\rightarrow t}$, ± 15%; ϕ_f, ± 10%. [b] Data from ref 1.

Conclusion

Activation energies of DAS and DPS obtained by fluorescence measurements thus reflect a strong temperature effect that incorporates at least two activated processes. One process is the trans-to-cis photoreaction leading to the cis product. The additional process (i) does not lead to the other isomer (hence excludes double bond twisting), (ii) is enhanced with increasing solvent polarity, and (iii) may be connected with excited state rotations around single bonds, probably those adjacent to the ethylenic double bond.

To our knowledge, only few stilbenes have been investigated in terms of activation energies by both fluorescence studies (ϕ_f or τ_f) and direct measurements of $\phi_{t\rightarrow c}$. Where this was done, the E_A values obtained are often in good aggreement (e.g., 4-cyanostilbene, 4,4′-dicyanostilbene, and *trans*-stilbene) but differ considerably in other cases (4-chlorostilbene and 4-nitrostilbenes).[1] In light of our results, E_A values obtained by fluorescence measurements alone should be viewed with much caution.

Experimental Section

If not stated otherwise, all measurements were performed in 1 × 1 cm quartz cuvettes in methanol. All solutions were used at concentrations of 2×10^{-5} mol/L and purged with argon for 5 min. Quantum yields of fluorescence were determined using quinine bisulfate ($\phi_f = 0.546$ in 1 N H_2SO_4) as a reference and a Hitachi-Perkin-Elmer MPF-2A fluorescence spectrometer. Quantum yields of isomerization were determined against the standard Aberchrome 540 ($\phi_{chem} = 0.20$ in toluene[17,18]) by means of a Kontron HPLC system coupled to a UV diode array detector. A reversed phase RP 18 column ($l = 25$ cm) was used ,and a water:acetonitrile gradient (90:10 to 1:99 in 40 min) served as the mobile phase. All solvents were spectrophotometric-grade (Uvasol, Merck). The samples were irradiated by an irradiation stand (Oriel) containing a HBO 500 mercury lamp (Osram) in combination with an 365 nm interference filter. Absorption spectra were recorded on a Hitachi U-3410 spectrophotometer. DAS was provided as hydrochloride by Aldrich Inc. and recrystallized several times in EtOH before use. After dissolution, 0.8% triethylamine was added. DPS was synthesized from DAS and *N*-phenyl-isothiocyanate according to Reid.[19] Purification was checked by HPLC.

The ground-state dipole moment of DPS was obtained by an ab initio DFT calculation (RHF 6-31G, HF-PW91) after an RHF 3-21G geometry optimization using Gaussian 98 on a SGI workstation.

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Supporting Information Available: Description of the procedure to obtain $\phi_{nr}{}^t + \phi_{nr}{}^c$ for the overall quantum yields of the nonradiative processes. This material is available free of charge via the Internet at http://pubs.acs.org.

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