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Invited feature article

Fate of photoexcited *trans*-aminostilbenes

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ABSTRACT

The decay pathways with relative quantum efficiencies for photoexcited *trans*-aminostilbenes in dilute organic solutions at ambient temperature are reviewed. Like the case of the parent *trans*-stilbene, fluorescence and the vinylene C=C torsion are two important decay pathways for *trans*-aminostilbenes. However, a new pathway, that is, formation of a TICT state by twisting the phenylene-amino C—N bond, dominates the excited-state deactivation of some *trans*-aminostilbenes in medium and/or highly polar solvents. On the basis of the quantum yields of fluorescence (Φ_f) and the *trans* → *cis* isomerization (Φ_{tc}) in solvents of different polarity, the TICT-forming activity of *trans*-aminostilbenes could be readily probed. The TICT states could be unambiguously characterized with ring-bridged model compounds, profiles of the emission spectra, and variable–temperature emission spectra. The interplay among fluorescence, the *trans* → *cis* isomerization, and the TICT state formation strongly depend on the nature and position of the amino group(s), the solvent polarity, and the other substituents that significantly perturb the steric and/or electronic properties. This provides a unique opportunity toward the design of novel fluorescent probes, light-emitting materials, and molecular switches.

1. Introduction

Trans-aminostilbenes are a class of π-donor–acceptor (D–A) systems that have been investigated as fluorescent probes [1–6], cell imaging dyes [7–9], and the active materials in a variety of optoelectronic devices such as organic light-emitting diodes [10,11], dye-sensitized solar cells [12–14], nonlinear optics [15–20], and molecular switches [21,22]. These applications are all associated with the electronically excited states, in which the lowest singlet excited state (S_1) possesses a significant degree of charge separation as a result of intramolecular charge–transfer (ICT) from the amino to the stilbene moiety upon photoexcitation. The polar ICT state corresponds spectroscopically to a high solvatofluorochromicity [23]. The ICT state could undergo two distinct types of adiabatic torsional relaxations: namely, the C=C torsion that forms a perpendicular ($^1p^*$) state and accounts for the *trans* → *cis* isomerization and the D–A torsion that forms a twisted intramolecular charge–transfer (TICT) state (Fig. 1). The interplay among fluorescence, photoisomerization, and TICT state formation strongly depends on the nature and position of the amino group, the steric and electronic impacts of substituents, and the solvent polarity. Since a fundamental understanding of the structure–activity relationship is essential for the design of novel aminostilbene-based dyes, our research group has been elucidating the effects of amino position, substituents, and solvent polarity on the fluorescence, photoisomerization, and TICT-forming activity of *trans*-aminostilbenes. This article will describe our previous efforts on this issue as well as related works by other groups. Unless otherwise mentioned, all the data and conditions for discussion in this article refer to those in dilute organic solutions and at ambient temperatures (295–298 K).

2. From *trans*-stilbene to *trans*-aminostilbenes: a general picture

Previous works on the parent *trans*-stilbene have paved an important foundation for understanding the photophysics and photochemistry of *trans*-aminostilbenes [24–28]. *Trans*-stilbene adopts a planar structure in the ground state, and torsions about the phenyl–vinylene C—C and the central vinylene C=C bonds encounter a barrier of ~4 and ~43 kcal/mol, respectively [29,30]. Photoexcitation of *trans*-stilbene ($^1t^*$) significantly weakens the bond order of the C=C bond such that the torsion barrier is largely diminished to 3.5 kcal/mol, which facilitates the *trans* → *cis* isomerization. As depicted in Fig. 2, the torsion reaches a conical intersection at an angle of ~90° called a phantom or perpendicular state ($^1p^*$). Internal conversion of the $^1p^*$ state leads to ^1p that is near the transition state of the *cis–trans* isomerization in the ground state. Because of the small energy difference between the *trans* and *cis* isomers, the driving force from ^1p to either isomer is

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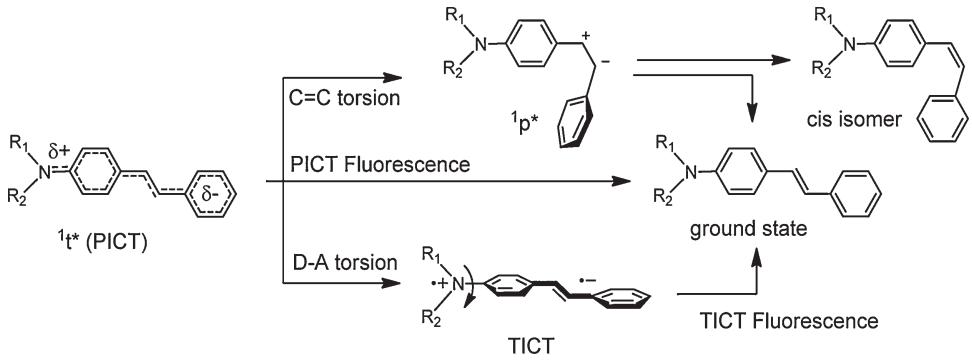

Fig. 1. Three major deactivated channels of photoexcited *trans*-aminostilbenes as represented by a para system.

similar (i.e., ~50% partition probability for each). Consequently, the determined *trans* → *cis* isomerization quantum yield (Φ_{tc}) is approximately half of the quantum efficiency for the C=C torsion (i.e., $\Phi_{\text{torsion of C=C}} \approx 2\Phi_{tc}$). The singlet-state C=C torsion dominates the photochemistry of *trans*-stilbene in solutions, resulting in low fluorescence quantum efficiencies ($\Phi_f \leq 5\%$). Constraint of the C=C torsion in favor of fluorescence has been demonstrated with *trans*-stilbene in spatially confined molecular hosts [31,32] or rigid media [33,34]. The sum of $\Phi_f + 2\Phi_{tc}$ is close to unity in all non-viscous solvents, indicating that other decay channels such as intersystem crossing ($^1t^* \rightarrow {}^3t^*$) and internal conversion ($^1t^* \rightarrow {}^1t$) of $^1t^*$ are relatively unimportant. Nevertheless, studies on photosensitized *trans*-stilbene show that the C=C torsion is even more favorable in the lowest triplet excited state (T_1) than in the S_1 state, as the $^3t^* \rightarrow {}^3p^*$ process is essentially barrierless and the intersystem crossing from $^3p^*$ to ^1p is much more efficient than that from $^3t^*$ to ^1t [25–28].

Substituent effects on the fluorescence and *trans* → *cis* isomerization of *trans*-stilbene are well-documented [25]. Substitutions on the phenyl ring generally retain the feature of low Φ_f and high Φ_{tc}, although the isomerization reaction might shift from S_1 to T_1 with certain substituents such as nitro, carbonyl, bromo, and iodo groups [35]. Regardless of the mechanism being singlet or triplet, the high efficiency of *cis–trans* photoisomerization renders stilbene systems good candidates as light-gated molecular switches [36,37]. On the other hand, substituents that suppress the C=C torsion in favor of fluorescence are desirable for applications as fluorescent probes or light-emitting materials. In this context, *trans*-aminostilbenes are particularly interesting, because certain amino groups could largely raise the singlet-state C=C torsion barrier such that the torsional process could become slower than the fluorescence decay (vide infra). However, introducing a strong electron-donating amino group to *trans*-stilbene simultaneously imposes an ICT character for this π system, which might induce a new decay pathway: namely, formation of a TICT state. In this context, whether a TICT state is effectively populated becomes the most critical question in understanding the photochemistry of *trans*-aminostilbenes.

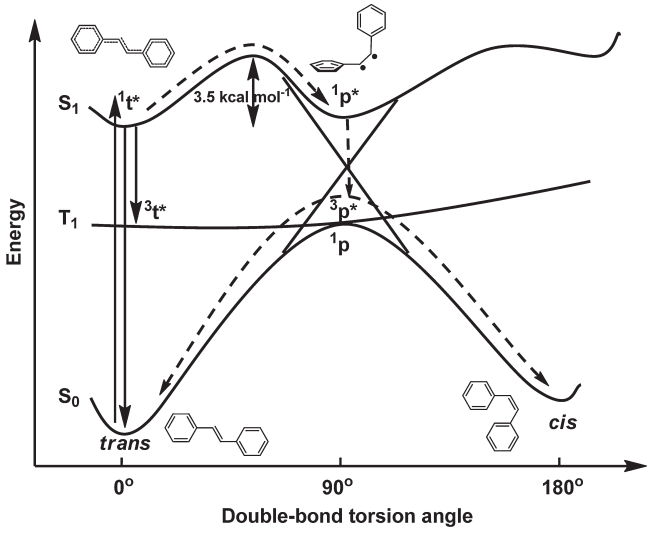

Fig. 2. Simplified potential energy surface diagram for the C=C torsion pathways of *trans*-stilbene.

3. TICT state of trans-aminostilbenes

3.1. Earlier TICT model of trans-aminostilbenes

The TICT model for D–A systems originated from the observation of dual emission at ~350 and ~550 nm for 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN) in acetonitrile (Chart 1) [38,39]. The short- and long-wavelength emission bands have been attributed to the so-called locally excited (LE) and ICT states, respectively, on the basis of the size and direction of transition dipole moments. Whereas the LE state has a dipole moment of ~9.7 D and the LE emission is short-axis polarized, the ICT state has a dipole moment as large as ~17 D with the emission being long-axis polarized [40]. The precursor–successor relationship between the LE and the ICT states is well established, but the structural nature of the ICT state has been controversial [41]. The two most often discussed models differ mainly in the torsion angle about the phenylene-amino C_{ph}—N bond: the ICT state that possesses a small torsion angle corresponds to a planar ICT (PICT) state, and the one with a large torsion angle is called a TICT state (Fig. 3). A PICT state

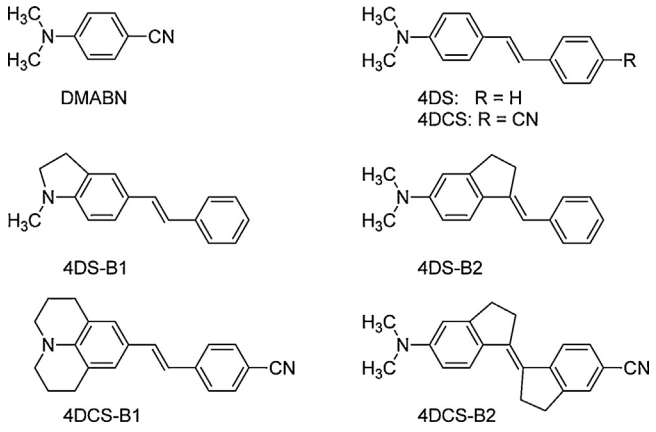

Chart 1. Structures of DMABN and *trans*-4-(*N*,*N*-dialkylamino)stilbenes.