Multisite Constrained Model of *trans*-4-(*N*,*N*-Dimethylamino)-4'nitrostilbene for Structural Elucidation of Radiative and Nonradiative Excited States

Cheng-Kai Lin, Yu-Fu Wang, Yuan-Chung Cheng,* and Jye-Shane Yang*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10617

Supporting Information

ABSTRACT: A constrained model compound of *trans*-4-(*N*,*N*-dimethylamino)-4'nitrostilbene (DNS), namely, compound DNS-B3 that is limited to torsions about the phenyl-nitro C–N bond and the central C=C bond, was prepared to investigate the structural nature of the radiative and nonradiative states of electronically excited DNS. The great similarities in solvent-dependent electronic spectra, fluorescence decay times, and quantum yields for fluorescence (Φ_f) and trans \rightarrow cis photoisomerization (Φ_{tc}) between DNS and DNS-B3 indicate that the fluorescence is from a planar charge-transfer state and torsion of the nitro group is sufficient to account for the



nonradiative decay of DNS. This conclusion is supported by TDDFT calculations on DNS-B3 in dichloromethane. The structure at the conical intersection for internal conversion is associated with not only a twisting but also a pyramidalization of the nitro group. The mechanism of the NO_2 torsion is discussed in terms of the effects of solvent polarity, the substituents, and the volume demand. The differences and analogies of the NO_2 - vs amino-twisted intramolecular charge-transfer (TICT) state of *trans*-aminostilbenes are also discussed.

INTRODUCTION

Conformational relaxation through torsions about a specific bond plays an important role in the excited-state deactivation of many chromophores. For *trans*-stilbene and its analogs, torsion about the central C=C bond (the τ torsion) in the excited state results in the *trans*-*cis* isomerization.¹ For some donor- π acceptor systems such as *N*,*N*-dimethylaminobenzonitrile (DMABN), torsion about the phenyl-amino C–N bond (the θ torsion) in polar solvents leads to a twisted intramolecular charge transfer (TICT) state that displays weak and largely Stokes-shifted fluorescence.² For nitroaromatics such as 4nitroaniline, twisting of the NO₂ group (the φ torsion) facilitates internal conversion (IC) of the lowest singlet excited (S₁) state and accounts for the ultrafast fluorescence quenching.³

Trans-4-(*N*,*N*-dimethylamino)-4'-nitrostilbene (DNS) is a nonlinear optical (NLO) dye⁴ that contains five (τ , θ , φ , α , and β) potential torsional modes in the excited states (Chart 1). The occurrence of the τ torsion can be readily detected due to the accompanied formation of the cis isomer. The τ torsion is significant for DNS in solvents of low polarity such as hexane and toluene but becomes negligible in polar solvents such as acetonitrile and methanol.⁵ The fluorescence quantum efficiency (Φ_f) of DNS is also largely dependent on the solvent polarity (e.g., $\Phi_f = 0.53$ in toluene but less than 0.01 in acetonitrile).⁵ Besides the τ torsion, one or more of the other torsional elements have been invoked for both the radiative and nonradiative decay channels of DNS. However, no new product is formed in association with these torsional relaxations. To date, the identity and the necessity of these torsional modes in



accounting for the observed photochemical behavior of DNS remain controversial.

Previous approaches toward an elucidation of the torsional relaxations of DNS include detection of the transient states with time-resolved spectroscopy,⁶ comparison of photochemical behavior with structurally constrained model compounds,^{5,7} and quantum chemical calculations.^{7–9} The possibility of nonradiative decays by twisting of the dimethylamino (θ) or the nitrophenyl (α) group was excluded on the basis of the similar photochemical properties of the model compounds DNS-B1⁵ and DNS-B2⁷ vs DNS (Chart 1). Radiative TICT states resulting from twisting of either the nitrophenyl (α) or the *N*,*N*-dimethylanilino (β) group and

```
Received:October 31, 2012Revised:March 16, 2013Published:March 21, 2013
```

ACS Publications © 2013 American Chemical Society

Scheme 1. Synthesis of DNS-B3



nonradiative decays due to twisting of the nitro (φ) group were proposed by Lapouyade, Rullière, and co-workers according to the transient absorption and Raman spectroscopy.⁶ The results of semiempirical calculations by Farztdinov and Ernsting indicate that the α , β , and φ torsions are all energetically favorable for DNS in polar solvents and that the α torsion is the best candidate to account for the fluorescence quenching.⁸ Recent time-dependent density functional theory (TDDFT) calculations led to either a planar or an α -twisted structure of S₁ depending on the functionals.⁹ Evidently, further studies are required to clarify the structural identity of the radiative and nonradiative states of DNS.

In this context, we have investigated the multisite (α , β , and θ) constrained model of DNS, i.e., DNS-B3 (Chart 1). We reasoned that the single-site constrained models DNS-B1 and DNS-B2 cannot distinguish the possible scenario: either one of the α , β , and θ torsions quenches the excited state of DNS, and an alternative torsion takes place even when the most preferred one is inhibited. As only the τ and φ torsions are allowed in DNS-B3, a comparison of the electronic spectra, Φ_{θ} and the trans \rightarrow cis isomerization quantum yield (Φ_{tc}) of DNS-B3 and DNS could provide a conclusive answer to the questions as to whether the highly polar fluorescing state of DNS is associated with torsional relaxations and whether the NO2-twisting in DNS is a viable nonradiative decay pathway in effectively competing with the fluorescence and the trans \rightarrow cis isomerization. TDDFT calculations on DNS-B3 were also performed to gain insights into these issues.

EXPERIMENTAL SECTION

General Methods. Electronic spectra were recorded at room temperature (23 \pm 1 °C). UV–visible spectra were measured on a Cary300 double beam spectrophotometer. Fluorescence spectra were recorded on an Edinburgh FLS920 spectrometer and corrected for the response of the detector. The optical density (OD) of all solutions was about 0.1 at the wavelength of excitation. A N₂-outgassed solution of coumarin 334 ($\Phi_f = 0.69$ in methanol)¹⁰ was used as standard for the fluorescence quantum yield determinations of compounds

under N2-outgassed solutions with solvent refractive index correction. An error of 10% is estimated for the fluorescence quantum yields. Fluorescence decays were also measured at room temperature with the use of the Edinburgh FLS920 spectrometer with a gated hydrogen arc lamp using a scatter solution to profile the instrument response function. The goodness of the nonlinear least-squares fit was judged by the reduced χ^2 value (<1.2 in all cases), the randomness of the residuals, and the autocorrelation function. The detailed method for measuring the quantum yields of photoisomerization has been described.¹¹ Briefly, optically dense N₂-outgassed solutions (1 \times 10⁻³ M) were excited at 400 nm using a 75 W Xe arc lamp and monochromator. The push-pull stilbene derivative trans-4-(2-(1-(4-methoxyphenyl)indolin-5-yl)vinyl)benzonitrile previously reported by our lab was used as a reference standard ($\dot{\Phi}_{tc} = 0.17$ in THF).¹² The extent of photoisomerization (<10%) was determined using HPLC analysis (Waters 600 Controller and 996 photodiode array detector, Thermo APS-2 Hypersil, heptane and ethyl acetate mixed solvent) without back-reaction corrections. The reproducibility error was <10% of the average. Density functional theory (DFT) calculations on the ground-state dipole moments of DNS and DNS-B3 were performed with the Gaussian 09 program¹³ at the B3LYP level of theory and 6-31G** basis set.¹⁴ TDDFT calculations on the excited-state properties of DNS-B3 were carried out using the GAMESS electronic structure package¹⁵ with the B3LYP functional and the 6-31G* basis set.¹⁴ In all the calculations, including geometry optimization and TDDFT calculations, the polarizable continuum model (PCM) was employed for the bulk solvent effects with the dichloromethane (DCM) solvent.¹⁶

Materials. Solvents for organic synthesis were reagent grade or HPLC grade, but all were HPLC grade for spectra and quantum yield measurements. All other compounds were purchased from commercial sources and were used as received. Analytical TLC was performed on commercial Merck plates coated with silica gel 60 F254. For flash chromatography, Merck Silica gel Si 60 (0.0603–0.2000 mm) was employed. DNS was prepared according to the literature.¹⁷

Scheme 1 illustrates the synthesis of DNS-B3 through a convergent route to construct the central C=C bond. As the C=C group is fully substituted and unsymmetrical, the conventional methods, such as the Wittig, Horner-Wadsworth-Emmons, and McMurry reactions, for olefin synthesis are impractical. Feringa and co-workers have demonstrated the utility of the Barton-Kellogg reaction, a coupling reaction between thicketone and dizao compounds, in preparing unsymmetrical and sterically hindered alkenes.¹⁸ This methodology was shown applicable to the preparation of DNS-B3. The nitro-containing diazo compound 1 and amino-containing thioketone 2 were prepared via intermediates 3-7 from 5aminoindane and via the intermediates 8-12 from 6bromoindole, respectively. Both 1 and 2 are unstable in the air and were generated in situ from the precursors for the coupling reaction. Detailed synthetic procedures, data of compound characterization, and NMR spectra of new compounds (Figures S1-S10) are provided in the Supporting Information. The trans configuration of DNS-B3 is verified with the COSY and NOESY spectra (Figure S11)

RESULTS AND DISCUSSION

Radiative Excited State. The absorption and fluorescence spectra of DNS-B3 in hexane and DCM are shown in Figure 1.



Figure 1. Normalized electronic absorption (curves a and b) and fluorescence (curves c and d) spectra of DNS-B3 in hexane (solid) and DCM (dash).

The absorption (λ_{abs}) and fluorescence (λ_f) maxima in hexane, toluene, THF, DCM, and acetonitrile (MeCN) are reported in Table 1. For comparison, the data⁵ of DNS are included. It should be noted that the window for the fluorescence detection with our instrument is only up to 850 nm, and the λ_f is larger

than 850 nm for DNS and DNS-B3 in MeCN. The intense long-wavelength absorption band is broadened and red-shifted in DCM vs hexane. The solvent effect on λ_f is even larger, indicating a high polarity for the fluorescent excited state.

The excited-state dipole moment (μ_e) of DNS-B3 can be estimated from the slope (m_i) of the solvatofluorochromic plot of the energies of the fluorescence maxima against the solvent parameter Δf according to eq 1¹⁹

$$\nu_{\rm f} = -[(1/4\pi\varepsilon_0)(2/hca^3)][\mu_{\rm e}(\mu_{\rm e} - \mu_{\rm g})]\Delta f + \text{constant}$$
(1)

where

$$\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - 0.5(n^2 - 1)/(2n^2 + 1)$$
 (2)

and

$$a = (3M/4N\pi d)^{1/3}$$
(3)

where $\nu_{\rm f}$ is the fluorescence maximum, $\mu_{\rm g}$ is the ground-state dipole moment, *a* is the solvent cavity (Onsager) radius, which was derived from the Avogadro number (*N*), molecular weight (*M*), and density (*d*), and ε , ε_0 , and *n* are the solvent dielectric constant, the vacuum permittivity, and the solvent refractive index, respectively. The value of $\mu_{\rm g}$ was calculated in the gas phase using the DFT algorithm for the optimized ground-state structure. For comparison, the $\mu_{\rm e}$ of DNS was redetermined with the same method. The detailed data of *a*, $m_{\rm fb} \mu_{e}$, and $\mu_{\rm g}$ are summarized in Table 2. The estimated $\mu_{\rm e}$ for DNS-B3 (22.1 D)

Table 2. Ground and Excited-State Dipole Moments for DNS and DNS-B3

compd	$a (Å)^a$	$m_{\rm f}~({\rm cm}^{-1})^b$	$\mu_{g} (D)^{c}$	μ_{e} (D)
DNS	4.91	23255	10.65	23.1 ± 0.9
DNS-B3	5.27	18516	10.02	22.1 ± 1.0

^{*a*}Onsager radius from eq 3 with d = 0.9 for DNS and DNS-B3. ^{*b*}Calculated based on eq 1. ^{*c*}Calculated by use of DFT (B3LYP/6-31G**).

is similar to that for DNS (23.1 D) in the fluorescent excited state. This demonstrates that there is no need to invoke the α , β , or θ torsion to account for the highly polar radiative state of DNS.

The red-shifted fluorescence for DNS-B3 vs DNS in the same solvent (e.g., $\Delta \nu_{\rm f} = 807 \ {\rm cm}^{-1}$ in DCM) is also an indication of a planar radiative state for DNS. Provided that the

Table 1. Photochemical Data for DNS and DNS-B3 in Solutions at Room Tempera	ture
---	------

compd	solvent	$\lambda_{abs} (nm)$	λ_{f}^{a} (nm)	$\Delta u_{1/2} \ (\mathrm{cm}^{-1})$	$\lambda_{0,0}{}^{b}$ (nm)	$\Delta u_{ m st}{}^c~(m cm^{-1})$	$\Phi_{ m f}$	$\Phi_{ m tc}{}^d$	$\Phi_{\rm f}$ + 2 $\Phi_{\rm tc}$
DNS ^e	c-Hex	420 ^f	501 ^f	3658 ^f	461 ^{<i>f</i>}	3849 ^f	0.33	0.28	0.89
	toluene	428	583				0.53	0.035	0.60
	THF	426	670				0.11	< 0.01 ^f	<0.13
	DCM	435	770	n.d. ^g	567 ^f	10001^{f}	0.008	< 0.01 ^f	< 0.03
	MeCN	435	>850				< 0.002	< 0.01 ^f	< 0.03
DNS-B3	n-Hex	440	562	3998	493	4934	0.21	0.38	0.97
	toluene	465	635	3176		5757	0.31	0.08	0.47
	THF	468	725	3132		7574	0.07	0.01	0.09
	DCM	469	821	n.d. ^g	630	8653	< 0.005	< 0.01	< 0.03
	MeCN	469	>850	n.d. ^g			< 0.005	< 0.01	< 0.03

^{*a*}Fluorescence data are from corrected spectra. ^{*b*}The value of $\lambda_{0,0}$ was obtained from the intersection of normalized absorption and fluorescence spectra. ${}^{c}\Delta\nu_{st} = \nu_{abs} - \nu_{fr} {}^{d}$ Containing 10% THF when determined in hexane (*n*-Hex) and acetonitrile (MeCN) by reason of solubility. ^{*e*}Data from ref 5 unless otherwise indicated. ^{*f*}Data from this work. ^{*g*}n.d. = not determined because of instrument limitation.

fluorescence of DNS was mainly contributed by a TICT state due to one of the α , β , and θ torsions, we would have expected a blue shift of the fluorescence spectrum for DNS-B3 vs DNS, as the torsion could not occur for DNS-B3. With the conclusion of a planar conformation for both DNS and DNS-B3 in the fluorescing state, the difference in their fluorescence maxima reflects the hyperconjugation effects of the additional bridged alkyl substituents in DNS-B3. A similar size of alkyl substituent effect on λ_{abs} should be observed if DNS and DNS-B3 had a similar planar conformation in the ground state. However, the red shift in λ_{abs} on going from DNS to DNS-B3 in DCM ($\Delta \nu_{abs} = 1667 \text{ cm}^{-1}$) is 2 times larger than that in λ_{f} . This indicates that the conformation of DNS is less planar than that of DNS-B3 in the ground state, which is consistent with a shallow potential energy surfaces (PES) along the α and the β torsion coordinates for trans-stilbenes in the electronic ground state.1,20

Nonradiative Decays. The Φ_f and Φ_{tc} for DNS and DNS-B3 in hexane, toluene, THF, DCM, and MeCN at room temperature are reported in Table 1. For both systems, the Φ_f is moderate in hexane and toluene but decreases to less than 1% in DCM and MeCN. The solvent effect on Φ_{tc} is even larger in which the moderate size in hexane (0.28–0.38) is decreased to 1% or less in THF and more polar solvents. The common excited-state behavior of DNS and DNS-B3 unambiguously shows that the discussion of torsional relaxation for DNS in the excited states can be restricted to the τ and φ torsions. To this end, the φ torsion is very likely responsible for the effective nonradiative decay of DNS in medium and highly polar solvents (vide infra). The α , β , or θ torsion is either not occurring at all or in an extent too small to have impact on the decay processes.

The relative size of Φ_f and Φ_{tc} for DNS-B3 vs DNS reflects a perturbation of the τ -torsion barrier by the bridged alkyl groups. DNS-B3 displays larger Φ_{tc} but lower Φ_f values than DNS does in hexane, toluene, and THF. It is very likely that the τ -torsion barrier is lower for DN-B3 than for DNS in S_1 so that the trans \rightarrow cis isomerization of DNS-B3 occurs not only in the triplet but also in the singlet excited states. We have previously shown that constraint of the α or the β torsion of *trans*-4-(*N*phenyleamino)stilbene by ring bridging lowers the barrier for the τ torsion to a significant extent, which results in an increase of the Φ_{tc} at the expense of Φ_f^{-21} In contrast, constraint of the θ torsion increases Φ_f by decreasing Φ_{tc}^{-21a} The observed ringbridging effect on Φ_f and Φ_{tc} was in the order $\alpha > \beta > \theta$. This trend would predict a larger Φ_{tc} and lower Φ_f for DNS-B3 vs DNS, which is indeed the case.

Two pieces of evidence show that no new emissive state is formed in association with the φ torsion for DNS-B3. The first one is the similar fluorescence band half-width ($\Delta \nu_{1/2} \approx 3000-$ 4000 cm⁻¹) in hexane and THF (Table 1). The presence of an emissive TICT state would have broadened the fluorescence spectra in THF vs hexane. The second evidence is the monoexponential fluorescence decay times and the independence of these decay times on emission wavelengths in hexane, toluene, and THF (Table S1, Supporting Information). In toluene, the observed fluorescence lifetime 2.2 \pm 0.1 ns for DNS-B3 is essentially the same as that $(2.3 \pm 0.1 \text{ ns})$ for DNS, again indicating a similar photodynamic behavior of the two compounds. As the nonemissive behavior of the τ -twisted excited state is a consequence of an ultrafast IC, the φ -twisted dark state could have the same origin. This is indeed supported by TDDFT calculations.

Molecular Modeling. The conclusion of a planar fluorescing state and the formation of a nonemissive NO_2 -twisted TICT state are further supported by TDDFT (B3LYP/ 6-31G*) calculations on DNS-B3 in DCM (PCM model). The optimized ground-state geometry is shown in Figure 2a in



Figure 2. Optimized structures of DNS-B3 in the (a) ground state, (b) radiative planar excited state, and (c) nonemissive NO_2 -twisted TICT excited state.

which the φ , α , τ , and β torsion angles are 0°, -12.7°, 178.3°, and -12.3° , respectively. The small α and β torsion angles can be attributed to the steric interactions between the bridged methylene/ethylene groups and the nearby phenyl C-H groups. The wag angle of the amino group, which is defined as $\theta_{wag} = (180 - \phi_{C28-N32-C35-C34})/2$ (Table S2, Supporting Information), is 19.6°, indicating a pyramidal geometry of the amino group. The TDDFT $S_0 \rightarrow S_1$ transition for the optimized ground-state geometry is at 566 nm with an oscillator strength of 0.81. The HOMO \rightarrow LUMO is the major configuration of the S1 state. As the HOMO and the LUMO are located mainly on the anilinovinyl and on the nitro groups, respectively, (Figure 3a), the Franck-Condon (FC) excited state exhibits a significant charge-transfer character, which is consistent with the large μ_e value. Optimization of the FC structure in the S₁ PES results in a rehybridization of the amino N atom to sp^2 -like and thus a planarization of the Nmethylindoline moiety (Figure 2b). Except for a more planar



Figure 3. Frontier orbitals of DNS-B3 in the (a) ground state (Franck–Condon transition) and (b) NO₂-twisted TICT excited state.

geometry of the amino group (amino wag angle $\theta_{wag} = 5.0^{\circ}$), this S₁ equilibrium structure is similar to the FC state in the φ , α , τ , and β torsion angles, which are 0°, -15.6°, 177.9°, and -14.6°, respectively. This nearly planar S₁ equilibrium state has an energy 3.2 kcal/mol lower than the FC state and corresponds to the radiative state with a theoretical emission maximum at ~646 nm.

Optimization of the S₁ state was also performed with initially guessed NO2-twisted conformations, which converged to a NO₂-twisted optimized structure (Figure 2c), corresponding to the NO2-twisted TICT state. The resulting equilibrium geometry exhibits not only the twisting feature but also a pyramidalization of the nitro group, evidenced by a nitro wag angle, defined as $\theta_{wag} = (180 - \phi_{C1-N43-O44-O45})/2$ (Table S2, Supporting Information), of 18.2°. We have performed geometry optimizations using unwagged and wagged NO2twisted initial guesses, and both converged to the same wagged structure, confirming the pyramidalization of the nitro group in the TICT state. This TICT state lies 5.3 kcal/mol lower in energy than the planar radiative state optimized with the FC geometry. The HOMO \rightarrow LUMO is the major configuration of the TICT S₁ state, and the LUMO is strongly localized on the nitro group due to the twisting and wagging of the NO₂ moiety. The more localized character of the TICT excited state explains the extra stabilization of TICT in polar solvents and the solvent-polarity dependent behavior of the photodynamics of DNS-B3. In addition, the different equilibrium geometries obtained from optimization of the FC vs NO2-twisted initial geometry indicates the presence of a barrier between these two optimized S_1 states. The TDDFT $S_0 \rightarrow S_1$ transition of the optimized TICT state is forbidden with a transition energy of only 8.5 kcal/mol, indicating that the structure is close to either a conical intersection or an avoided crossing point. The small S_0-S_1 energy gap at the TICT optimized geometry can be attributed to a highly destabilized structure for the ground state, which is higher by ~33.5 kcal/mol compared to the optimized ground state (Table S3, Supporting Information). As rotation of the nitro group to a perpendicular position from the optimized planar ground state only costs 9.3 kcal/mol in the ground-state PES, the high ground-state energy at the S₁ TICT equilibrium geometry must be due to pyramidalization of the nitro group or structural changes in the aminostilbene backbone, particularly the planarization of the amino group. Noticeably, the planarization of the N-methylindoline moiety only destabilizes the ground state by ~ 3 kcal/mol in the S₁planar state (Table S3, Supporting Information). Thus, the nitro pyramidalization must function as a critical promoter for the ultrafast IC of the NO2-twisted TICT state. These features reconcile the nonemissive character of the TICT state and suggest a detailed deactivation channel following photoexcitation of DNS-B3 in polar solvents. Figure 4 depicts a simplified PES along the amino planarization and the nitro torsion/wag coordinates for the excited state of DNS-B3 in DCM. A PES profile similar to Figure 4 was also reported for twisting the nitro group in 1-(p-nitrophenyl)-2-(hydroxymthyl)pyrrolidine (p-NPP) in polar solvents.^{3d}

Photodynamic Model for DNS. Figure 5 shows our proposed deactivation mechanism for electronically excited DNS in polar solvents. The PES along the τ torsional coordinate follows the conventional one-bond-flip mechanism for *trans*-stilbenes.¹ The τ torsion can occur either in S₁ or T₁, but the triplet mechanism is expected to dominate, as it is known that the nitro group facilitates a rapid intersystem



Figure 4. Simplified scheme for the potential energy surfaces along the φ torsion/wag and the amino planarization coordinates for the singlet excited state of DNS-B3 in DCM.



Figure 5. Schematic potential energy surface diagrams associated with the φ and the τ torsions in accounting for the relaxation mechanism of DNS in polar solvents. The φ torsion is accompanied with a pyramidalization (wagging) of the nitro N atom. The curved arrows denote the major (in red) and the minor (in green) decay pathways. The structures show a twist angle at 90°, corresponding to the states that internal conversion takes place.

crossing.²² Indeed, Gruen and Görner reported that the triplet mechanism prevails the trans—cis photoisomerization of DNS.⁵ As the conical intersection is located at a torsion angle near 90°, corresponding to the transition state of the thermal cis—trans isomerization, conformational relaxation toward the trans and the cis form from the transition state has a similar (i.e., 50%) probability. Consequently, the quantum efficiency of the τ torsion (Φ_{τ}) can be estimated as $2\Phi_{tc}$. The parameter $\Phi_{f} + 2\Phi_{tc}$ is 0.89 for DNS and 0.97 for DNS-B3 in hexane and indicates that the excited decay is mainly due to fluorescence and the τ torsion, and the φ torsion is negligible. However, the $\Phi_{f} + 2\Phi_{tc}$ value decreases dramatically to 0.60 in toluene, to 0.11 in THF, and to less than 0.03 in DCM and MeCN. Evidently, the φ torsion-induced IC is more favorable in more polar solvents.

Our previous studies have shown that formation of a TICT state is viable for *trans*-aminostilbenes having sufficiently strong push-pull character.^{12,21a} Dual fluorescence or unresolved broadened fluorescence spectra were observed for the amino-twisted systems in polar solvents. The nonemissive nature of the NO₂-twisted TICT states of DNS and DNS-B3 is different

from the emissive, albeit weak, amino-twisted TICT states of DMABN and *trans*-aminostilbenes.^{2c} One possible explanation is a very quick IC for the NO₂-twisted TICT states, as is the case of 1-(*p*-nitrophenyl)-2-(hydroxymthyl)pyrrolidine (within 10 ps).^{3d} Another difference between the amino- and the NO₂-twisted TICT states of *trans*-aminostilbenes is their quantum efficiency in toluene, a low-polarity but polarizable solvent. Whereas the formation of an amino-twisted TICT state is negligible in toluene, the fact of $\Phi_f + 2\Phi_{tc} \leq 0.6$ for DNS and DNS-B3 indicates the occurrence of the φ torsion to a significant extent (40–50%). The latter might be attributed to a small difference in molecular dipole for the NO₂-twisted TICT state and the fluorescent precursor, as is the case of 2-(4-*N*,*N*-dimethylamino-7-nitrofluorenone (about 2 D).²³

It should be noted that the volume demand for the twisting of a nitro group is relatively small as compared to that for a dimethyamino or an aryl group (e.g., the α , β , and θ torsions in DNS). This might explain the moderate but not high Φ_f (0.3) for DNS in glassy MTHF and ethanol at 77 K,⁵ as the volumeconserving NO₂ torsion is incompletely inhibited in the solvent glass. Although the other torsions cannot be completely excluded, both the φ and τ torsions are sufficient to account for the nonradiative decay behavior of DNS in S₁ under all conditions.

The mechanistic concept shown in Figure 5 also allows one to understand the difference between DNS and nitrosubstituted *trans*-stilbenes such as *trans*-4-nitrostilbene (NS) and *trans*-4,4'-dinitrostilbene (NSN). Both NS and NSN display a high value of Φ_{tc} (0.38–0.39) in polar solvents such as methanol.²⁴ Without the electron-pushing amino group, the NO₂ in NS and NSN might undergo only the pyramidalization (wagging) but not the torsion, as is the case of nitrobenzene²⁵ vs nitroaniline.^{3b} Without an accessible low-energy TICT state near a conical intersection, their deactivation is as expected dominated by trans–cis isomerization.

CONCLUSIONS

The great similarity in the excited-state behavior for DNS and the multisite bridged model DNS-B3 provides a piece of unambiguous evidence in favor of the twisting of the nitro group (the φ torsion) as a nonradiative decay channel and a planar fluorescent charge-transfer state for DNS in polar solvents. This mechanistic insight is important not only for DNS but also for other push—pull nitroaromatics and should be valuable for molecular designs toward novel fluorescent probes, molecular switches, and NLO materials.

ASSOCIATED CONTENT

S Supporting Information

Detailed synthetic schemes, compound characterization data, and ¹H and ¹³C NMR spectra for all new compounds; the Lippert–Mataga plots of DNS and DNS-B3; fluorescence decay times for DNS-B3; equilibrium DFT structures of DNS-B3; selected DFT structural parameters of DNS-B3; calculated electronic properties of DNS-B3; *xyz*-coordinates of DFT structures; complete ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: (+886) 233661649 (J.-S.Y.); (+886)233669788 (Y.-C.C.). E-mail: jsyang@ntu.edu.tw (J.-S.Y.); yuanchung@ntu. edu.tw (Y.-C.C.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Science Council of Taiwan for financial support. High-resolution ESI mass analyses were performed by Instrumentation Center of NTU. The DFT-derived μ_e values provided by Dr. C. Prabhakar, the Φ_{tc} value of DNS in THF provided by Mr. Che-Jen Lin, and the computing time granted by the National Center for High-Performance Computing and the Computing Center of NTU are acknowledged. This paper is dedicated to Prof. Frederick D. Lewis on the occasion of his 70th Birthday for his pioneer work in the photophysics and photochemistry of stilbenes.

REFERENCES

(1) (a) Saltiel, J.; Charlton, J. L. Rearrangements in Ground and Excited States; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3. (b) Waldeck, D. H. Photoisomerization Dynamics of Stilbenes. Chem. Rev. 1991, 91, 415–436. (c) Görner, H.; Kuhn, H. J. Cis-trans Photoisomerization of Stilbenes and Stilbene-Like Molecules. Adv. Photochem. 1995, 19, 1–117.

(2) (a) Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W. Structural Changes Accompanying Intramolecular Electron Transfer: Focus on Twisted Intramolecular Charge-Transfer States and Structures. *Chem. Rev.* 2003, 103, 3899–4031. (b) Rettig, W.; Maus, M. Conformational Analysis of Molecules in Excited States; Waluk, J., Ed.; Wiley-VCH: New York, 2000. (c) Rettig, W. Charge Separation in Excited States of Decoupled Systems-TICT Compounds and Implications Regarding the Development of New Laser Dyes and the Primary Processes of Vision and Photosynthesis. *Angew. Chem., Int. Ed.* 1986, 25, 971–988.

(3) (a) Kovalenko, S. A.; Schanz, R.; Farztdinov, V. M.; Hennig, H.; Ernsting, N. P. Femtosecond Relaxation of Photoexcited *para*-Nitroaniline: Solvation, Charge Transfer, Internal Conversion and Cooling. *Chem. Phys. Lett.* **2000**, 323, 312–322. (b) Farztdinov, V. M.; Schanz, R.; Kovalenko, S. A.; Ernsting, N. P. Relaxation of Optically Excited *p*-Nitroaniline: Semiempirical Quantum-Chemical Calculations Compared to Femtosecond Experimental Results. *J. Phys. Chem. A* **2000**, *104*, 11486–11496. (c) Rafiq, S.; Yadav, R.; Sen, P. Femtosecond Excited-State Dynamics of 4-Nitrophenyl Pyrrolidinemethanol: Evidence of Twisted Intramolecular Charge Transfer and Intersystem Crossing Involving the Nitro Group. *J. Phys. Chem. A* **2011**, *115*, 8335–8343. (d) Ghosh, R.; Palit, D. K. Ultrafast Dynamics of the Excited States of 1-(*p*-Nitrophenyl)-2-(hydroxymethyl)pyrrolidine. *J. Phys. Chem. A* **2012**, *116*, 1993–2005.

(4) Marder, S. R.; Kippelen, B.; Jen, A. K. Y.; Peyghambarian, N. Design and Synthesis of Chromophores and Polymers for Electrooptic and Photorefractive Applications. *Nature* **1997**, *388*, 845–851.

(5) Gruen, H.; Görner, H. Trans \rightarrow Cis Photoisomerization, Fluorescence, and Relaxation Phenomena of *trans*-4-Nitro-4'-(dialkylamino)stilbenes and Analogues with a Naonrotatable Amino Group. J. Phys. Chem. **1989**, 93, 7144–7152.

(6) (a) Oberlé, J.; Abraham, E.; Jonusauskas, G.; Rullière, C. Study of the Intramolecular Charge-Transfer (ICT) Process in 4-Dimethylamino-4'-nitrostilbene by Picosecond Time-Resolved CARS. J. Raman. Spectrosc. 2000, 31, 311–317. (b) Oberlé, J.; Jonusauskas, G.; Abraham, E.; Lapouyade, R.; Rullière, C. Time-Resolved Charge Transfer in "Push-Pull" Stilbenes. Bull. Chem. Soc. Jpn. 2002, 75, 1041–1047.

(7) Lapouyade, R.; Kuhn, A.; Letard, J. F.; Rettig, W. Multiple Relaxation Pathways in Photoexcited Dimethylaminonitro- and Dimethylaminocyano-stilbenes. *Chem. Phys. Lett.* **1993**, *208*, 48–58.

(8) Farztdinov, V. M.; Ernsting, N. P. Solvent Dependence of Structure and Electronic Properties in the Ground and First Excited Singlet State of 4-Dimethylamino-4'-Nitrostilbene (DANS)-Semiempirical Calculations. *Chem. Phys.* **2002**, *277*, 257–270.

(9) Petsalakis, I. D.; Georgiadou, D. G.; Vasilopoulou, M.; Pistolis, G.; Dimotikali, D.; Argitis, P.; Theodorakopoulos, G. Theoretical Investigation on the Effect of Protonation on the Absorption and Emission Spectra of Two Amine-Group-Bearing, Red "Push–Pull" Emitters, 4-Dimethylamino-4'-nitrostilbene and 4-(dicyanomethylene)-2-methyl-6-p-(dimethylamino)styryl-4H-pyran, by DFT and TDDFT calculations. *J. Phys. Chem. A* 2010, *114*, 5580–5587.

(10) Reynolds, G. A.; Drexhage, K. H. New Coumarin Dyes with Rigidized Structure for Flashlamp-Pumped Dye Lasers. *Opt. Commun.* **1975**, *13*, 222–225.

(11) Huang, G.-J.; Cheng, C.-W.; Hsu, H.-Y.; Prabhakar, C.; Lee, Y.-P.; Diau, E. W.-G.; Yang, J.-S. Effects of Hydrogen Bonding on Internal Conversion of GFP-like Chromophores: The *para*-Amino Systems. *J. Phys. Chem. B* **2013**, *117*, 2695–2704.

(12) The compound is abbreviated as **2OMB** in the article: Yang, J.-S.; Liau, K.-L.; Hwang, C.-Y.; Wang, C.-M. Photoinduced Singleversus Double-Bond Torsion in Donor-Acceptor-Substituted *trans*-Stilbenes. *J. Phys. Chem. A* **2006**, *110*, 8003–8010.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(14) (a) Lee, C.; Yang, W.; Parr, R. Development of the Colic–Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789. (b) Becke, A. D. Densityfunctional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (c) Hariharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. *Theor. Chim. Acta* **1973**, *28*, 213–222.

(15) Schmidt, M.; Baldridge, K.; Boatz, J.; Elbert, S.; Gordon, M.; Jensen, J.; Koseki, S.; Matsunaga, N.; Nguyen, K.; et al. General Atomic and Molecular Electronic Structure System. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

(16) (a) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. J. Phys. Chem. A **1998**, 102, 1995–2001. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, Structures, and Electronic Properties of Molecules in Solution with the C-PCM Solvation Model. J. Comput. Chem. **2003**, 24, 669–681.

(17) Wu, C.; Wei, J.; Tian, D.; Feng, Y.; Miller, R. H.; Wang, Y. Molecular Probes for Imaging Myelinated White Matter in CNS. J. Med. Chem. 2008, 51, 6682–6688.

(18) (a) Pijper, D.; van Delden, R. A.; Meetsma, A.; Feringa, B. L. Acceleration of a Nanomotor: Electronic Control of the Rotary Speed of a Light-Driven Molecular Rotor. *J. Am. Chem. Soc.* 2005, 127, 17612–17613. (b) Carroll, G. T.; London, G.; Landaluce, T. F.; Rudolf, P.; Feringa, B. L. Adhesion of Photon-Driven Molecular Motors to Surfaces via 1,3-Dipolar Cycloadditions: Effect of Interfacial Interactions on Molecular Motion. ACS Nano 2011, 5, 622–630.

(19) Baumann, W.; Bischof, H.; Fröhling, J. C.; Brittinger, C.; Rettig, W.; Rotkiewicz, K. Considerations on the Dipole Moment of Molecules Forming the Twisted Intramolecular Charge Transfer State. J. Photochem. Photobiol., A 1992, 64, 49–72.

(20) Han, W.-G.; Lovell, T.; Liu, T.; Noodleman, L. Density Functional Studies of the Ground- and Excited-State Potential-Energy Curves of Stilbene cis-trans Isomerization. *ChemPhysChem* **2002**, *3*, 167–178.

(21) (a) Yang, J.-S.; Liau, K.-L.; Wang, C.-M.; Hwang, C.-Y. Substituent-Dependent Photoinduced Intramolecular Charge Transfer in *N*-Aryl-Substituted *trans*-4-Aminostilbenes. *J. Am. Chem. Soc.* 2004, 126, 12325–12335. (b) Yang, J.-S.; Lin, C.-K.; Lahoti, A. M.; Tseng, C.-K.; Liu, Y.-H.; Lee, G.-H.; Peng, S.-M. Effect of Ground-State Twisting on the trans \rightarrow cis Photoisomerization and TICT State Formation of Aminostilbene. *J. Phys. Chem. A* 2009, 113, 4868–4877.

(22) (a) Hurley, R.; Testa, A. C. Triplet-State Yield of Aromatic Nitro Compounds. J. Am. Chem. Soc. 1968, 90, 1949–1952.
(b) Collado-Fregoso, E.; Zugazagoitia, J. S.; Plaza-Medina, E. F.; Peon, J. Excited-State Dynamics of Nitrated Push-Pull Molecules: The

Importance of the Relative Energy of the Singlet and Triplet manifolds. J. Phys. Chem. A 2009, 113, 13498-13508.

(23) Mondal, J. A.; Sarkar, M.; Samanta, A.; Ghosh, H. N.; Palit, D. K. Charge-Transfer-Induced Twisting of the Nitro Group. *J. Phys. Chem. A* **2007**, *111*, 6122–6126.

(24) Schultefrohlinde, D.; Görner, H. Cis–Trans Photoisomerization of 4-Nitrostilbenes. *Pure. Appl. Chem.* **1979**, *51*, 279–297.

(25) Takezaki, M.; Hirota, N.; Terazima, M.; Sato, H.; Nakajima, T.; Kato, S. Geometries and Energies of Nitrobenzene Studied by CAS-SCF Calculations. *J. Phys. Chem. A* **1997**, *101*, 5190–5195.