ARTICLE

OBC
www.rsc.org/obc

The photochemical characteristics of aromatic enediyne compounds substituted with electron donating and electron withdrawing groups

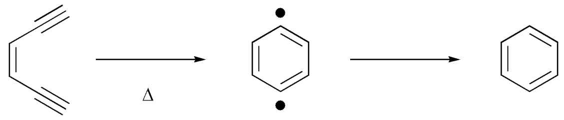
Yoshihiro Miki, Atsuya Momotake and Tatsuo Arai*
University of Tsukuba, tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan.
E-mail: arai@chem.tsukuba.ac.jp; Fax: 81-298-53-4521; Tel: 81-298-53-4315

Received 27th May 2003, Accepted 24th June 2003
First published as an Advance Article on the web 9th July 2003

trans- and *cis*-1-(4-Dimethylaminophenyl)-6-(4-nitrophenyl)hex-3-ene-1,5-diynes (*trans*- and *cis*-DANE) were synthesized and their photochemical properties were studied. The absorption spectra of *trans*-DANE red-shifted compared with the parent compound bisphenylethynylethene (BEE) due to intramolecular charge transfer. The fluorescence spectra, Stokes shift, fluorescence lifetime, fluorescence quantum yield, and quantum yield of *trans*-to-*cis* photoisomerization of *trans*-DANE showed strong dependence upon the solvent polarity in the less-polar region. No fluorescence emission from *trans*-DANE was observed in medium-polar and polar solvents. The quantum yield of *cis*-to-*trans* isomerization was almost solvent independent. The donor–acceptor substituents shifted the equilibrium between the *trans* perpendicular triplet state and the *trans* planar triplet state to the *trans* triplet state, and resulted in an increase in the triplet lifetime. Comparison of the photochemical properties of *trans*-DANE with *trans*-4-dimethylamino-4′-nitrostilbene (DANS) suggests that *trans*-DANE is a possible fluorescent probe in the non-polar region.

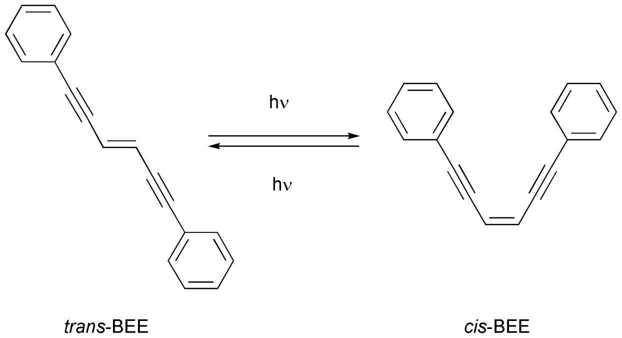
Introduction

Enediyne compounds have been greatly investigated in the areas of biological activity and physical properties. In the area of biological activity, they have been investigated as antitumor antibiotics. For example, the drugs esperamicin, calichemicin, and dynemicin, each of which possesses an enediyne unit, have been shown to produce a highly reactive aromatic 1,4-biradical intermediate by heating (Scheme 1).[1–4] Furthermore, the intermediate has been shown to cause the cutting of DNA chains. Since enediyne compounds have an olefin part, they can undergo isomerization.[5] Moreover, enediyne compounds are expected to have applications as non-linear optical materials when donor–acceptor substituents are introduced, because the conjugation may be spread over the whole molecule. Thus, enediyne compounds are investigated in many fields, but reports of photoreactions are few. We decided to synthesize enediyne compounds and to investigate the character of the exited state and the photochemical reactivity.



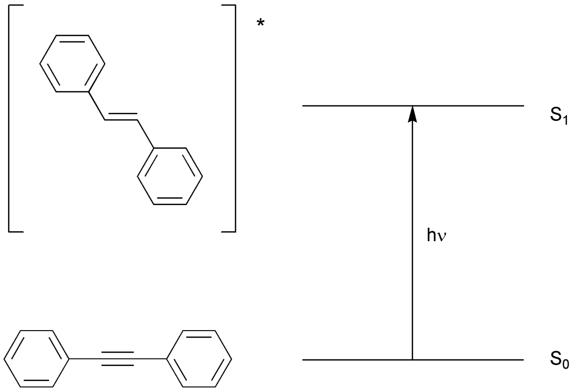
Scheme 1 Generation of a 1,4-biradical intermediate from an enediyne.

Previously we reported the photochemical reactivity of aromatic enediyne compounds (bisphenylethynylethene; BEE, Scheme 2).[6] *cis–trans* Photoisomerization took place as the main feature. For example, on irradiation with 328 nm light, BEE gave a *trans*-to-*cis* isomer ratio at the photostationary state (pss) of $([t]/[c])_{pss} = 44/56$ in benzene with a quantum yield of *cis*-to-*trans* and *trans*-to-*cis* isomerization of 0.27 and 0.17, respectively. In addition we have observed fluorescence emission both from *cis* and *trans* isomers of BEE peaking at 360–380 nm even at room temperature with high quantum yields of 0.31 and 0.42, respectively. Furthermore, the excited triplet state was observed. Thus, aromatic enediyne compounds show an interesting photochemical behaviour.



Scheme 2 *trans-cis* Photoisomerization of BEE.

As an example of the photochemistry of a double bond, stilbene is known to undergo *cis–trans* photoisomerization. As an example of the structural characteristic of the photoexcited state of the triple bond, Hamaguchi and co-workers proposed, from CARS spectra, that the excited singlet state of diphenylacetylene takes a *trans*-bent structure with a centre of symmetry (Scheme 3).[7] Thus, double and triple bonds show very interesting photochemical behaviour, and because aromatic enediyne compounds have the photochemical characteristics of

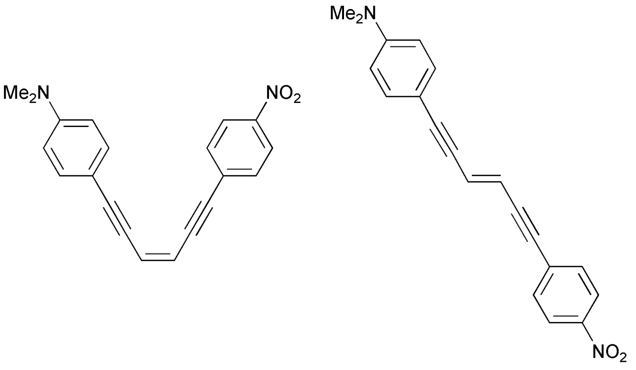


Scheme 3 Structure of excited singlet state of diphenylacetylene.

DOI: 10.1039/b305816f

stilbene and diphenylacetylene, their investigation is considered to be significant.

In this paper, we wish to report the photoisomerization and fluorescence properties of aromatic enediyne compounds substituted with an electron donating and an electron withdrawing group (1-(4-dimethylaminophenyl)-6-(4-nitrophenyl)-hex-3-ene-1,5-diyne; DANE, Scheme 4). The intramolecular charge transfer interaction may affect the reactivity of an excited state.



***cis*-DANE** **trans-DANE**

Scheme 4 Structures of DANEs.

The photoisomerization and fluorescence properties of stilbenes substituted with a donor and an acceptor group at the *para* position of the phenyl ring have already been studied.[8–13] A large solvent effect on the fluorescence spectra observed in a stilbene with dimethylamino and nitro substituents at the *para* position (DANS) indicated the important role of the twisted intramolecular charge transfer state for the deactivation from the excited state. The enediyne compound is closely related to the stilbene, and tetra-substituted analogues at the olefinic C=C double bond of enediyne have already been studied and reported previously.[14,15] However, disubstituted enediyne compounds at the C=C double bond with a donor and an acceptor group at the adjacent phenyl group have not been studied yet. We wish to explore the excited state behaviour of donor–acceptor substituted enediyne compounds closely related to the stilbene from a basic interest.

Results and discussion

UV Absorption and fluorescence spectra

cis- and *trans*-DANEs were synthesized from *N*,*N*-dimethylaniline and 4-bromonitrobenzene (Scheme 5). Fig. 1 shows a typical example of the absorption spectra of *cis*- and *trans*-DANEs in cyclohexane at room temperature. The band shapes and absorption maxima of both *cis*- and *trans*-isomers exhibited only weak solvent dependence (Table 1).

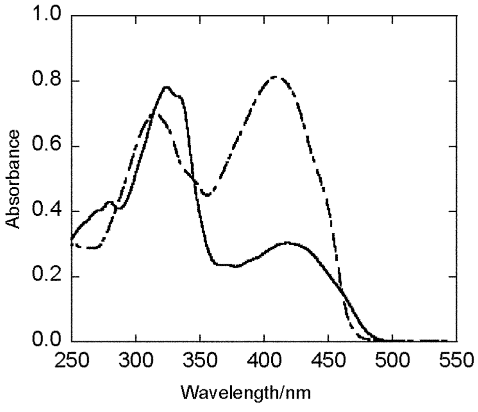


Fig. 1 UV absorption spectra of *trans*-DANE (dot–dash line) and *cis*-DANE (solid line).

Table 1 Absorption maxima, fluorescence maxima and Stokes shift of DANEs

Solvents	λ_{abs}/nm		λ_{fl}/nm	$\Delta\nu$/cm^{-1}
	cis	*trans*	*trans*	*trans*
Cyclohexane	324	315	469	3000
	418	410	499	
Benzene	333	325	581	6600
	423	421		
Dichloromethane	335	327		
	427	422		
Acetonitrile	329	320		
	415	411		

Fig. 2 shows the fluorescence and fluorescence excitation spectra of *trans*-DANE in cyclohexane and benzene at room temperature. The fluorescence maxima appeared at 469 nm and 499 nm with vibrational progression in cyclohexane, while the fluorescence spectrum was broadened and red shifted in benzene. No fluorescence emission from *trans*-DANE was observed in dichloromethane and acetonitrile. The fluorescence quantum yields and the fluorescence lifetimes were determined to be 0.33 and 0.55 ns in cyclohexane, 0.25 and 2.4 ns in benzene, respectively. As listed in Table 1, the Stokes shifts between the absorption maximum and fluorescence maximum for *trans*-DANE were calculated to be 3000 and 6600 cm^{-1} in cyclohexane and in benzene, respectively.

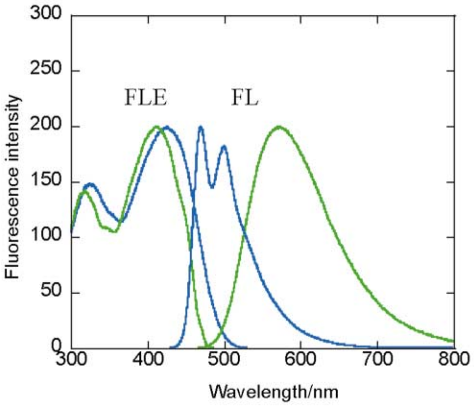
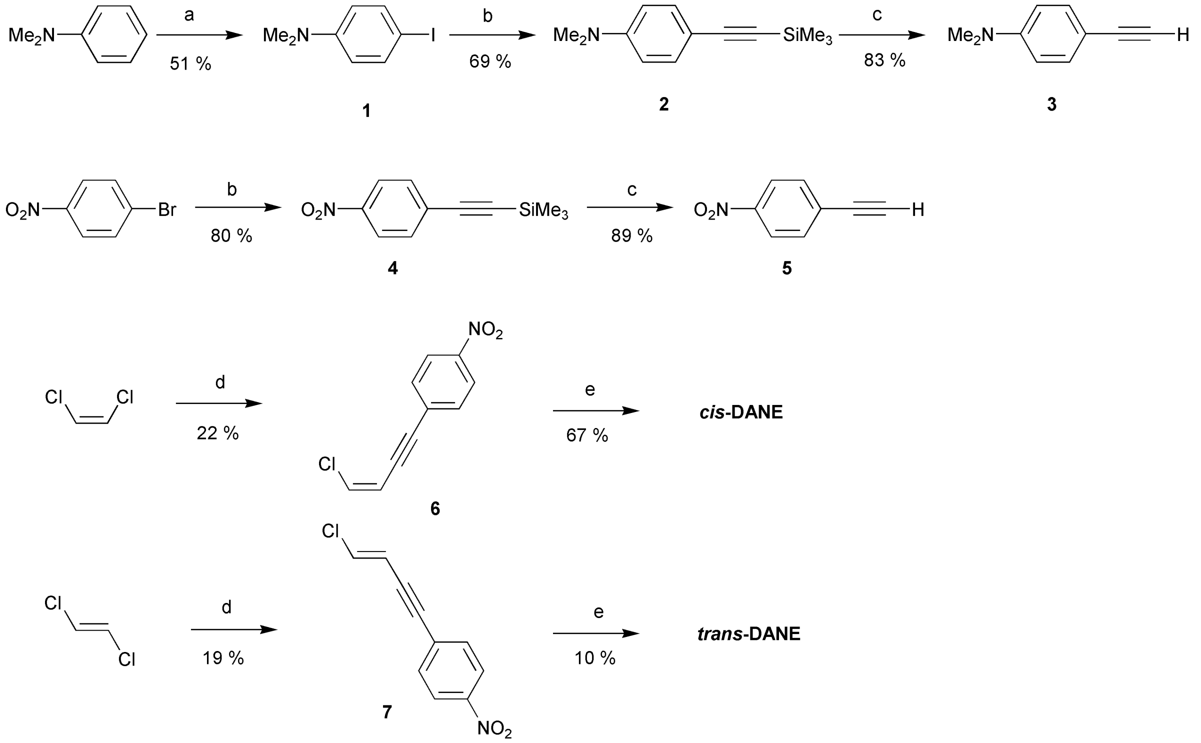


Fig. 2 Fluorescence (FL) and fluorescence excitation (FLE) spectra of *trans*-DANE in cyclohexane (blue) and in benzene (green).

trans-DANE exhibited fluorescence spectra in non-polar and slightly polar solvents, while *cis*-DANE did not give any fluorescence in any solvent. The fact that no fluorescence was observed in the spectrum of *cis*-DANE is in contrast to the observation of fluorescence emission for the *cis* isomer of BEE in benzene.[6] The present finding indicates that the introduction of electron donating and electron accepting substituents at the *para* position remarkably changes the excited singlet state behaviour of the *cis*-isomer of aromatic enediyne compounds.

Fluorescence spectral change in mixed solvents

Fig. 3 shows the fluorescence spectral change with changing ratio of dichloromethane : cyclohexane at room temperature. The fluorescence maximum shifted to a longer wavelength with increasing solvent polarity. The fluorescence intensity slightly increased with an increasing ratio up to 4% dichloromethane, and then drastically decreased with a further increase in the ratio of dichloromethane. The fluorescence emission had almost disappeared when the ratio of dichloromethane was more than 60%. Inset in Fig. 3 shows the change of the Stokes shift with increasing ratio of dichloromethane in cyclohexane. The solvent polarity in the less polar region strongly affected their Stokes shift. The fluorescence quantum yields with



Scheme 5 *Reagents and conditions:* (a) NaI, NaOCl, MeOH; (b) trimethylsilylacetylene, CuI, $Pd(PPh_3)_2Cl_2$, benzene, Et_3N; (c) K_2CO_3, MeOH, ether; (d) **5**, CuI, PPh_3, $Pd(dba)_2$, benzene, n-$BuNH_2$; (e) **3**, CuI, PPh_3, $Pd(dba)_2$, benzene, n-$BuNH_2$.

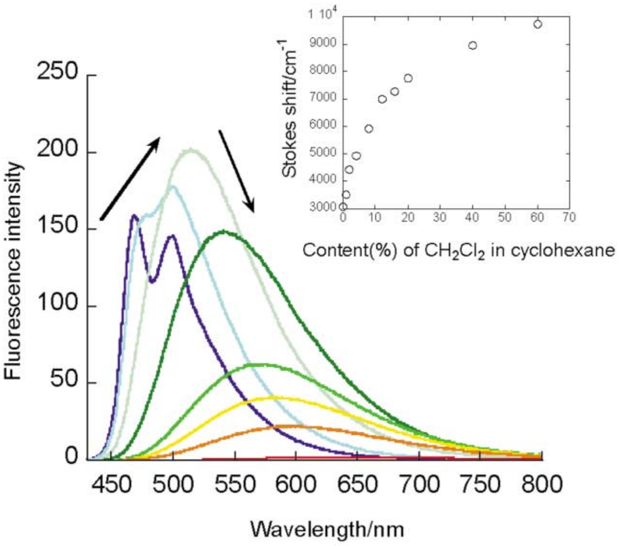


Fig. 3 Fluorescence spectra of *trans*-DANE in mixed solvents of dichloromethane–cyclohexane. Dichloromethane content (%): 0% (dark blue), 1% (blue), 4% (light blue), 8% (green), 12% (yellowish green), 16% (yellow), 20% (orange), 40% (red) and 60% (dark red). Inset shows the change of the Stokes shift values with increasing ratio of dichloromethane in cyclohexane

Table 2 Fluorescence maxima, Stokes shift and fluorescence quantum yield of *trans*-DANE in a mixed solvent (dichloromethane–cyclohexane)

CH_2Cl_2 Content (vol %)	λ_{fl}/nm	$\Delta\nu$/cm^{-1}	Φ_{fl}
0	469, 499	3000	0.33
1	479, 500	3500	0.37
2	501	4400	0.40
4	514	4900	0.42
8	541	5900	0.31
12	576	7000	0.13
16	584	7300	0.085
20	601	7800	0.046
40	647	8900	0.004
60	682	9700	0.0004

changing ratio of dichloromethane–cyclohexane are summarized in Table 2. These results indicate that a polar solvent may stabilize the intramolecular charge transfer state to give fluorescence emission at longer wavelengths and to accelerate the deactivation from the excited singlet state. The Stokes shifts increased with increasing solvent polarity. In the solution containing 60% of CH_2Cl_2 in cyclohexane, the Stokes shift became as large as 9700 cm^{-1}. These results indicate that electronic structure and/or molecular structure greatly depend on the solvent polarity. The solvent effect on the fluorescence spectra observed for DANS has been explained by the mechanism: the intramolecular charge transfer state (ICT) or/and twisted intramolecular charge transfer state (TICT) has been proposed for the deactivation from the excited singlet state of DANS.[8–9] Therefore, the intramolecular charge transfer state (ICT) is supposed to be involved in the radiative deactivation from the singlet excited state.

cis–trans Photoisomerization

Fig. 4 shows the change in the absorption spectra during the photoisomerization of *trans*-DANE in cyclohexane at room temperature. On photoirradiation, the absorption maximum of *trans*-DANE shifted to a longer wavelength and the absorbance intensity decreased, indicating the occurrence of isomerization to the *cis* isomer. The photostationary state $([t]/[c])_{pss}$ was 10/90 in cyclohexane. The $([t]/[c])_{pss}$ value is related to the ratio of the extinction coefficient at the excitation wavelength of *cis*- (ε_c) and *trans*-DANE (ε_t) and that of the isomerization quantum yield from *trans*-to-*cis* ($\Phi_{t \longrightarrow c}$) and *cis*-to-*trans* direction ($\Phi_{c \longrightarrow t}$). The value of $\varepsilon_c/\varepsilon_t$ at 365 nm is 1.3/3.3. Therefore, the ratio of $\Phi_{t \longrightarrow c}/\Phi_{c \longrightarrow t}$ is estimated to be 0.78/0.22.

Table 3 summarizes the quantum yields of *cis*-to-*trans* and *trans*-to-*cis* isomerization as well as the photostationary state in various solvents. The quantum yield of *trans*-to-*cis* isomerization was 0.13 in cyclohexane and decreased with increasing solvent polarity. The values were almost constant in benzene, CH_2Cl_2, and acetonitrile. The quantum yields of *cis*-to-*trans* isomerization had almost the same value among the solvents

Table 3 Quantum yields of photoisomerization and the *trans*/*cis* ratio at the photostationary state

Solvent	$\Phi_{t\text{-to-}c}$	$\Phi_{c\text{-to-}t}$	$([t]/[c])_{\mathrm{pss}}$
Cyclohexane	0.13	0.037	10/90
Benzene	0.049	0.044	46/54
Dichloromethane	0.038	0.063	39/61
Acetonitrile	0.034	0.037	25/75

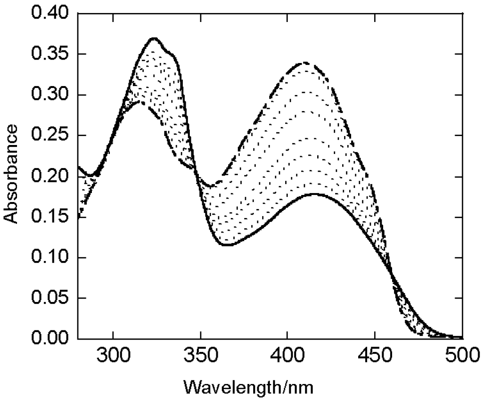


Fig. 4 Change of absorption spectrum of *trans*-DANE on irradiation with 365 nm light in cyclohexane under argon: before (dash-dot line) and after irradiation (solid line).

examined in these experiments, *ca.* 0.04–0.05. Therefore, the low quantum yield of *cis*-to-*trans* isomerization is one of the reasons for the considerably high *cis* isomer composition of the photostationary state in cyclohexane. The $\Phi_{t \longrightarrow c}$ value decreased with increasing solvent polarity to decrease the *cis* isomer composition at the photostationary state. The above results strongly indicate that the excited state behaviour of DANE was affected by solvent polarity and the change is remarkable between cyclohexane and benzene. This excited state property is due to the donor–acceptor substituent groups on the enediyne.

Transient absorption spectra

On 308 nm laser excitation, the T-T absorption spectra for *trans*-DANE were observed in benzene under argon at room temperature (Fig. 5). The decay observed at 500–800 nm was assigned to the T-T absorption spectra and the rising component at 420 nm was assigned to the production of *cis*-DANE. The triplet lifetime was determined to be 2 µs at 600 nm. The rising time constant at 420 nm was also 2 µs, which was in accord with the decaying time constant. The concomitant increase in the absorbance of *trans*-DANE with the decay of the T-T absorption spectra indicates that the *cis*–*trans* isomerization took place in the excited triplet state after undergoing intersystem crossing. Similarly, permanent bleaching was observed in the transient spectra starting from the *trans*-DANE due to the photochemical *trans*-to-*cis* isomerization. The triplet lifetime was 200 ns under air and 70 ns under oxygen, respectively. Thus, the quenching rate constant was estimated to be $2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$.

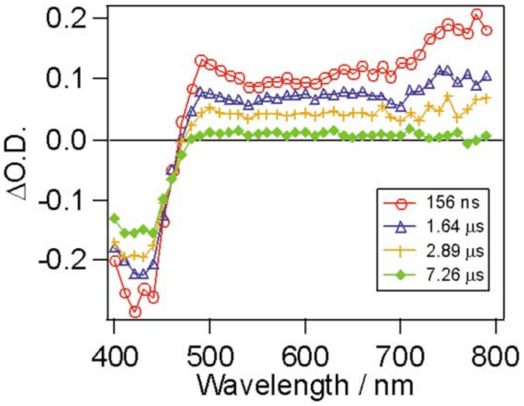


Fig. 5 Transient absorption spectra of *trans*-DANE in benzene, observed on laser flash photolysis with a focused 308 nm laser beam.

The triplet lifetime for BEE was determined to be 370 ns in benzene, where the planar triplet state and perpendicular triplet state were expected to be equilibrated with a ratio of 86 : 14.[6] The considerably long lifetime observed for DANE indicates that the equilibrium is shifted to the planar conformation in DANE compared to BEE. One can roughly estimate the ratio of the planar triplet state and perpendicular triplet state ($[^3p^*]/[^3t^*]$) from the observed triplet lifetime and the decay rate constant from $^3p^*$ ($k_{\mathrm{dp}} = 2 \times 10^7\ \mathrm{s^{-1}}$) and $^3t^*$ ($k_{\mathrm{dt}} = 2 \times 10^4\ \mathrm{s^{-1}}$).[16] Thus, ($[^3p^*]/[^3t^*]$) was estimated to be 1/40, indicating that most of the triplet state exists as the planar conformation. The ($[^3p^*]/[^3t^*]$) value is 1/6 in BEE. Therefore introduction of the donor and acceptor groups at the *para* position in BEE resulted in a considerable change of the equilibrium towards the planar conformation to increase the triplet lifetime.

Comparison with push–pull stilbenes

The basic photochemical properties of *trans*-DANE were compared with *trans*-4-dimethylamino-4′-nitrostilbene (DANS), which is a typical photoresponsive chromophore with a conjugated linkage of electron-accepting and electron-donating groups.[8–11] Two points are noteworthy.

i) Although the distance between electron-donating and accepting groups on *trans*-DANE is longer than that of DANS due to the two conjugated triple bonds, absorption maxima of DANE and DANS in various solvents appeared mostly in the same region; 410–422 nm for *trans*-DANE and 410–440 nm for DANS. The absorption spectra of *trans*-DANE showed less solvent dependence than that of DANS. If it exhibits large hyperpolarizabilities without a red-shift in more polar solvents, then *trans*-DANE will be potentially useful for non-linear optical applications.

ii) The fluorescence quantum yield of DANS decreases with increasing solvent polarity but is still measurable even in polar solvents such as acetone or DMF, while that of *trans*-DANE was falling off drastically to be 0.0004 in dichloromethane–cyclohexane = 60/40. Thus, the fluorescence change of *trans*-DANE is more sensitive than that of DANS in the non-polar region, suggesting *trans*-DANE is a possible fluorescent probe in the non-polar region.

In order to shed light on the properties of the excited singlet state of DANE, either ICT or TICT depending on the solvent polarity, we should prepare model compounds and examine their fluorescence properties. Thus, much further work is required on this point. However, the above results that the solvent effect on the fluorescence properties of *trans*-DANE is different from that of DANS indicates that ICT rather than TICT plays an important role for the deactivation from the excited single state of *trans*-DANE.

Conclusion

In summary, absorption spectra of *trans*-DANE, having an donor–acceptor substituent at the *para* position of BEE, red-shifted compared with the parent compound BEE due to intramolecular charge transfer. The absorption spectra of *trans*-DANE showed weak solvent dependence. The fluorescence spectra, Stokes shift, fluorescence lifetime, fluorescence quantum yield, and quantum yield of *trans*-to-*cis* photoisomerization were affected by a small change of solvent polarity in the less-polar region. No fluorescence emission was observed in medium-polar and polar solvents. The quantum yield of *cis*-to-*trans* isomerization was almost solvent independent. The triplet state of *trans*-DANE was observed on direct excitation with 308 nm laser light in benzene. The donor–acceptor substituent shifted the equilibrium between the *trans* perpendicular triplet state and the *trans* planar triplet state to the *trans* triplet state, and resulted in an increase of the triplet lifetime.

Experimental

Materials

Preparation of compounds **1**–**5** are similar to those reported in other papers.[17–19]

***N*,*N*-Dimethyl-4-iodoaniline (1).** Aqueous sodium hypochlorite (61.0 g, 82.0 mmol) was added dropwise over 2 h to the solution of *N*,*N*-dimethylaniline (6.91 g, 57.0 mmol) and sodium iodide (9.57 g, 63.0 mmol) in methanol (140 ml) at 10 °C. The mixture was stirred at 10–15 °C for 4 h, then allowed to warm up to room temperature for 12 h. After the reaction was complete, the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous NH_4Cl, then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (eluent: hexane) to give 7.24 g (51%) of **1** as yellow crystals. δ_H (400 MHz; $CDCl_3$; Me_4Si) 7.46 (2H, d, *J* 8.4 Hz, ArH), 6.49 (2H, d, *J* 8.8 Hz, ArH), 2.92 (6H, s, CH_3).

1-(4-Dimethylaminophenyl)-2-trimethylsilylethyne (2). A mixture of **1** (7.24 g, 29.3 mmol), trimethylsilylacetylene (2.16 g, 22.0 mmol), $[PdCl_2(PPh_3)_2]$ (890 mg, 1.27 mmol), and CuI (450 mg, 2.37 mmol) in triethylamine (150 ml) was stirred at 40 °C for 12 h. After the reaction was complete, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with saturated aqueous NH_4Cl followed by saturated aqueous NaCl, then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (eluent: hexane–$CHCl_3$ = 9 : 1) to give 3.24 g (69%) of **2** as yellow crystals. δ_H (400 MHz; $CDCl_3$; Me_4Si) 7.32 (2H, d, *J* 8.8 Hz, ArH), 6.57 (2H, d, *J* 8.8 Hz, ArH), 2.95 (6H, s, CH_3), 0.21 (9H, s, CH_3).

4-Dimethylaminophenylethyne (3). A mixture of **2** (2.28 g, 10.5 mmol) and K_2CO_3 (14.5 g, 105 mmol) in MeOH–ether (180 ml–130 ml) was stirred at room temperature overnight. After the reaction was complete, the reaction mixture was poured into water and extracted with ether. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo* to give 1.27 g (83%) of **3** as a yellow liquid. δ_H (400 MHz; $CDCl_3$; Me_4Si) 7.36 (2H, d, *J* 9.2 Hz, ArH), 6.61 (2H, d, *J* 8.8 Hz, ArH), 2.97 (7H, s, CH_3 and H).

1-(4-Nitrophenyl)-2-trimethylsilylethyne (4). A mixture of 4-bromonitrobenzene (5.00 g, 24.8 mmol), trimethylsilylacetylene (2.91 g, 29.7 mmol), $[PdCl_2(PPh_3)_2]$ (344 mg, 0.49 mmol), and CuI (93 mg, 0.49 mmol) in triethylamine–benzene (100 ml–100 ml) was stirred at 60 °C overnight. After the reaction was complete, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with saturated aqueous NH_4Cl followed by saturated aqueous NaCl, then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (eluent: hexane) to give 4.31 g (80%) of **4** as yellow crystals. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.15 (2H, d, *J* 8.8 Hz, ArH), 7.57 (2H, d, *J* 8.4 Hz, ArH), 0.25 (9H, s, CH_3).

4-Nitrophenylethyne (5). A mixture of **4** (4.31 g, 19.7 mmol), K_2CO_3 (6.87 g, 49.7 mmol) in MeOH (100 ml) and ether (75 ml) was stirred at room temperature for 2 h. After the reaction was complete, the reaction mixture was poured into water and extracted with ether. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo* to give 2.58 g (89%) of **5** as yellow crystals. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.18 (2H, d, *J* 8.8 Hz, ArH), 7.62 (2H, d, *J* 9.2 Hz, ArH), 3.34 (1H, s, H).

***cis*-1-Chloro-4-nitrophenylbut-1-ene-3-yne (6).** A mixture of **5** (2.05 g, 13.9 mmol), *cis*-dichloroethylene (5.40 g, 55.7 mmol), $Pd(dba)_2$ (335 mg, 0.58 mmol), PPh_3 (460 mg, 1.75 mmol), and CuI (334 mg, 1.75 mmol) in degassed *n*-$BuNH_2$ (63 ml) and benzene (108 ml) was stirred at room temperature overnight. After the reaction was complete, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with saturated aqueous NH_4Cl, then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (eluent: hexane–$CHCl_3$ = 4 : 1) to give 633 mg (22%) of **6** as yellow crystals. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.21 (2H, d, *J* 8.8 Hz, ArH), 7.64 (2H, d, *J* 8.8 Hz, ArH), 6.57 (1H, d, *J* 8.0 Hz, olefinic proton), 6.12 (1H, d, *J* 7.2 Hz, olefinic proton).

***trans*-1-Chloro-4-(4-nitrophenyl)but-1-ene-3-yne (7).** A mixture of **5** (500 mg, 3.40 mmol), *trans*-dichloroethylene (1.32 g, 13.6 mmol), $Pd(dba)_2$ (64.9 mg, 0.11 mmol), PPh_3 (89.2 mg, 0.34 mmol), and CuI (64.8 mg, 0.34 mmol) in degassed *n*-$BuNH_2$ (12 ml) and benzene (18 ml) was stirred at room temperature overnight. After the reaction was complete, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with saturated aqueous NH_4Cl, then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (eluent: hexane–$CHCl_3$ = 4 : 1) to give 134 mg (19%) of **7** as yellow crystals. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.20 (2H, d, *J* 8.8 Hz, ArH), 7.58 (2H, d, *J* 8.8 Hz, ArH), 6.74 (1H, d, *J* 13.4 Hz, olefinic proton), 6.18 (1H, d, *J* 13.8 Hz, olefinic proton).

***cis*-1-(4-Dimethylaminophenyl)-6-(4-nitrophenyl)hex-3-ene-1,5-diyne (*cis*-DANE).** A mixture of **3** (1.27 g, 1.36 mmol), **6** (633 mg, 3.06 mmol), $Pd(dba)_2$ (1.66 g, 2.89 mmol), PPh_3 (2.66 g, 10.2 mmol), and CuI (1.08 g, 5.69 mmol) in degassed *n*-$BuNH_2$ (40 ml) and benzene (110 ml) was stirred at room temperature overnight. After the reaction was complete, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with saturated aqueous NH_4Cl, then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (eluent: hexane–$CHCl_3$ = 4 : 1) to give 650 mg (67%) of *cis*-DANE as orange crystals. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.21 (2H, d, *J* 8.8 Hz, ArH), 7.64 (2H, d, *J* 8.8 Hz, ArH), 7.37 (2H, d, *J* 8.8 Hz, ArH), 6.65 (2H, d, *J* 8.8 Hz, ArH), 6.22 (1H, d, *J* 10.4 Hz, olefinic proton), 5.98 (1H, d, *J* 10.8 Hz, olefinic proton), 3.01 (6H, s, CH_3); Elemental analysis. Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86; Found: C, 76.39; H, 5.44; N, 8.58%.

***trans*-1-(4-Dimethylaminophenyl)-6-(4-nitrophenyl)hex-3-ene-1,5-diyne (*trans*-DANE).** A mixture of **3** (468 mg, 3.23 mmol), **7** (333 mg, 1.61 mmol), $Pd(dba)_2$ (614 g, 1.07 mmol), PPh_3 (984 mg, 3.75 mmol), and CuI (400 mg, 2.10 mmol) in degassed *n*-$BuNH_2$ (14 ml) and benzene (40 ml) was stirred at room temperature overnight. After the reaction was complete, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with saturated aqueous NH_4Cl, then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (eluent: hexane–$CHCl_3$ = 4 : 1) to give 50 mg (10%) of *trans*-DANE as orange crystals. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.17 (2H, d, *J* 8.8 Hz, ArH), 7.56 (2H, d, *J* 8.8 Hz, ArH), 7.33 (2H, d, *J* 8.8 Hz, ArH), 6.62 (2H, d, *J* 8.8 Hz, ArH), 6.38 (1H, d, *J* 16.0 Hz, olefinic proton), 6.16 (1H, d, *J* 16.4 Hz, olefinic proton), 2.99 (6H, s, CH_3); Elemental analysis. Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86; Found: C, 75.09; H, 5.37; N, 8.66%.

Measurements

Absorption and fluorescence spectra were measured on a Shimazu UV-1600 and on a Hitachi F-4500 fluorescence spectrometer, respectively. Quantum yields of fluorescence were determined by using anthracene ($\Phi_f = 0.27$) as an emission standard. Fluorescence lifetimes were determined with a Horiba NAES-1100 time resolved spectrofluorometer. Quantum yields of isomerization were determined with 366 nm light from a 400 W high-pressure mercury lamp through UV-35 and UV-360 filters. The sample solution was deaerated with bubbling argon and irradiated for 3–5 min to keep the conversion to within 10%. Light intensity was determined by tris(oxalate)ferrate(III) actinometry. The concentration of each isomer was determined by high performance liquid chromatography through a column (Toso CN-80TS) eluting with ethyl acetate–*n*-hexane = 1 : 99. Laser flash photolyses were performed by using an excimer laser (Lambda Physik LPX-100, 308 nm, 20 ns fwhm) as excitation light source and a pulsed xenon arc (Ushio UXL-159) was used as a monitoring light source. A photomultiplier (Hamamatsu R-928) and a storage oscilloscope (Iwatsu TS-123) were used for the detection.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) and the 21 Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government and by the Asahi Glass Foundation.

References

1 Y. Sugihara, Y. Uesawa, Y. Takahashi, J. Kuwahara, J. Golik and T. W. Doyle, Nucleotide-specific cleavage and minor-groove interaction of DNA with esperamicin antitumor antibiotics, *Proc. Natl. Acad. Sci. USA*, 1989, **86**, 7672–7676.

2 N. Zein, M. Poncin, R. Nilakantan and G. A. Ellestad, Calicheamicin γ1I and DNA: molecular recognition process responsible for site-specificity, *Science*, 1989, **244**, 697–699.

3 Y. Sugihara, T. Arakawa, M. Uesugi, T. Shiraki, H. Ohkuma and M. Konishi, Reductive and nucleophilic activation products of dynemicin A with methyl thioglycolate. A rational mechanism for DNA cleavage of the thiol-activated dynemicin A, *Biochemistry*, 1991, **30**, 2989–2992.

4 M. Hirama, T. Gomibuchi, K. Fujiwara, Y. Sugiura and M. Uesugi, Synthesis and DNA cleaving abilities of functional neocarzinostatin chromophore analogs. Base discrimination by a simple alcohol, *J. Am. Chem. Soc.*, 1991, **113**, 9851–9853.

5 B. Koenig, E. Schofield, P. Bubenitschek and P. G. Jones, Synthesis and photoinduced *cis-trans* isomerization of diaryl enediyne chromophores, *J. Org. Chem.*, 1994, **59**, 7142–7143.

6 H. Sakakibara, M. Ikegami, K. Isagawa, S. Tojo, T. Majima and T. Arai, Novel finding of the effect of triple bond on the photochemical *cis-trans* isomerization of C=C double bond, *Chem. Lett.*, 2001, 1050–1051.

7 T. Ishibashi, H. Okamoto and H. Hamaguchi, Picosecond transient infrared spectra and structure of S_1 diphenylacetylene in solution, *Chem. Phys. Lett.*, 2000, **325**, 212–218.

8 H. Gruen and H. Görner, *Trans* ⟶ *cis* Photoisomerization, fluorescence, and relaxation phenomena of *trans*-4-nitro-4′-(dialkylamino)stilbenes and znalogues with a nonrotatable amino group, *J. Phys. Chem.*, 1989, **93**, 7144–7152.

9 R. Lapouyade, A. Kuhn, J. F. Letard and W. Retting, Multiple relaxation pathways in photoexcited dimethylaminonitro- and dimethylaminocyano-stilbenes, *Chem. Phys. Lett.*, 1993, **208**, 48–58.

10 H. Görner, Photophysics and photochemistry of *trans*-4-nitrostilbenes and *trans*-2,4-dinitrostilbenes: Effect of intramolecular charge transfer, *Ber. Bunsenges. Phys. Chem.*, 1998, **102**, 726–737.

11 H. Görner, The *cis-trans* isomerization of nitrostilbenes XV: Mixed singlet and triplet mechanism for *trans* ⟶ *cis* photoisomerization of 4-nitro-4′-dialkylamino-stilbnenes in non-polar solvents, *J. Photochem. Photobiol. A*, 1987, **40**, 325–339.

12 G. Gurzadyan and H. Görner, Picosecond transient absorption spectroscopy of *trans*-4-R-4′-nitrostilbenes with R: OMe, NH_2 and NMe_2, *Chem. Phys. Lett.*, 2000, **319**, 164–172.

13 V. Papper, D. Pines, G. Likhtenshtein and E. Pines, Photophysical characterization of *trans*-4,4′-disubtituted stilbenes, *J. Photochem. Photobiol. A*, 1997, **111**, 87–96.

14 R. E. Martin, J. Bartek, F. Diederich, R. R. Tykwinski, E. C. Meister, A. Hilger and H. P. Luthi, Photochemical *trans-cis* isomerization of donor/acceptor-substituted (*E*)-hex-3-ene-1,5-diynes (1,2-diethynylethenes, DEEs) and 3,4-diethynylhex-3-ene-1,5-diynes (tetraethynylethenes, TEEs), *J. Chem. Soc, Perkin Trans. 2*, 1998, 233–241.

15 F. Diederich, Carbon-rich acetylenic scaffolding: rods, rings and switches, *Chem. Commun.*, 2001, 219–227.

16 T. Arai and K. Tokumaru, Photochemical one-way adiabatic isomerization of aromatic olefins, *Chem. Rev.*, 1993, **93**, 23–39.

17 R. R. Tykwinski, M. Schreiber, R. P. Carlon, F. Diederich and V. Gramlich, *Helv. Chim. Acta*, 1996, **79**, 2249–2281.

18 J. A. John and J. M. Tour, Synthesis of polyphenylene derivatives by thermolysis of enediynes and dialkynylaromatic monomers, *Tetrahedron.*, 1997, **53**, 15515–15534.

19 K. J. Edgar and S. N. Falling, An efficient and selective method for the preparation of iodophenols, *J. Org. Chem.*, 1990, **55**, 5287–5291.