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Photochemistry of Linear-Shaped Phenylacetylenyl- and (Phenylacetylenyl)phenylacetylenyl-Substituted Aromatic Enediynes

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The series of linear-shaped phenylacetylenyl- and (phenylacetylenyl)phenylacetylenyl-substituted aromatic enediynes **1**−**3** were synthesized as pure trans and cis isomers and their photochemistry explored. With expansion of the π-electron system, the absorption spectra red-shifted and the molar extinction coefficients dramatically increased up to 122000 M^{-1} cm^{-1} for *trans*-**3**. The absorption spectra of *cis*-**2** and *cis*-**3** consisted of two independent absorption bands. The fluorescence quantum yields of the molecules were high, even for the cis isomers ($\Phi_f = 0.39-0.61$). The fluorescence decay of each of the compounds was analyzed as a single exponential and the wavelength dependence of time constants was not observed, indicating a single emitting state in all cases. All isomers exhibited mutual cis−trans photoisomerization. The quantum yield of both trans-to-cis and cis-to-trans photoisomerization considerably decreased in **2** and **3**, presumably due to an increased number of photochemical processes that yield nonreactive excited species and which result in nonradiative deactivation. Three energy minima exist in the excited triplet state, where the energy of planar conformation decreased with the extension of the phenyl acetylenyl chain, resulting in the promotion of nonradiative processes without conformational change.

Introduction

Enediynes have been widely investigated, especially in the area of antitumor antibiotics. The drugs esperamicin, calichemicin, and dynemicin, for example, all possess an aliphatic endiyne unit and produce a reactive 1,4-biradical aromatic intermediate upon heating.[1−4] Aromatic enediynes, on the other hand, are usually thermally stable and have been known to exhibit unique photochemical properties in organic solvents. Previously we reported the photochemical reactivity of aromatic enediyne bisphenylethynylethene (**BEE**) (Figure 1a).[5] **BEE** gives efficient fluorescence emission from both the cis and trans isomers and undergoes intersystem crossing in addition to cis−trans photoisomerization. Furthermore, three energy minima exist in the triplet state potential surface where the planar triplet state (^{3}trans* and ^{3}cis*) and the perpendicular triplet state (^{3}p*) are equilibrated. The fluorescence spectra, Stokes shift, fluorescence lifetime, fluorescence quantum yield, and quantum yield of trans-to-cis photoisomerization for the "push−pull" aromatic enediynes *trans*- and *cis*-1-(4-dimethylaminophenyl)-6-(4-nitrophenyl)hex-3-ene-1,5-diynes (**DANE**) that contain both electron-withdrawing and electron-donating groups on the phenyl rings (Figure 1b) were found to exhibit a strong dependence on solvent polarity in the less-polar region.[6] The effects of methoxy substituents on the phenyl ring of the cis isomer of enediynes were also explored; ortho-substituted compounds (Figure 1b) showed a red shift of the fluorescence even though crystallographic analysis suggests that the single bond connecting the phenyl ring and carbon−carbon triple bond takes a twisted conformation.[7] Furthermore, both lipophilic[8] and amphiphilic[9] enediyne-cored dendrimers were prepared as pure cis and trans isomers. All dendrimers were fluorescent with fluorescence quantum yields of 0.10−0.66 and underwent efficient photochemical isomerization in THF with quantum yields of 0.18−0.50. Fluorescence and triplet lifetimes were strongly affected by dendrimer generation and solvent polarity.

On the basis of these results, we focused our attention on the photochemical properties of the linear-shaped aromatic enediynes **1**−**3**, where the π-electron system of the enediyne should be expanded due to introduction of phenylacetylenyl or (phenylacetylenyl)phenylacetylenyl units in the para position (Figure 1c). The effects of extending the π-electron system on the photochemistry of aromatic enediynes have not been studied but are of interest from the viewpoint of construction of molecules with new emissive and/or reactive properties.

Experimental Section

Apparatus. Sample solutions were prepared in benzene (Kanto Chemical) and deoxygenated by bubbling highly purified argon (>99.999%) through a needle. Fluorescence and excitation spectra were measured with an Hitachi F-4500 fluorescence spectrophotometer using a 1 cm ×1 cm quartz cuvette. Absorption spectra were recorded with a Shimadzu UV-1600 spectrophotometer. Fluorescence decay measurements were performed using a time-correlated single-photon counting method. The apparatus was assembled based on the method previously described.[10,11] Excitation at 410 nm was achieved using a diode laser (PicoQuant, LDH-P-C- 405) driven by a power control

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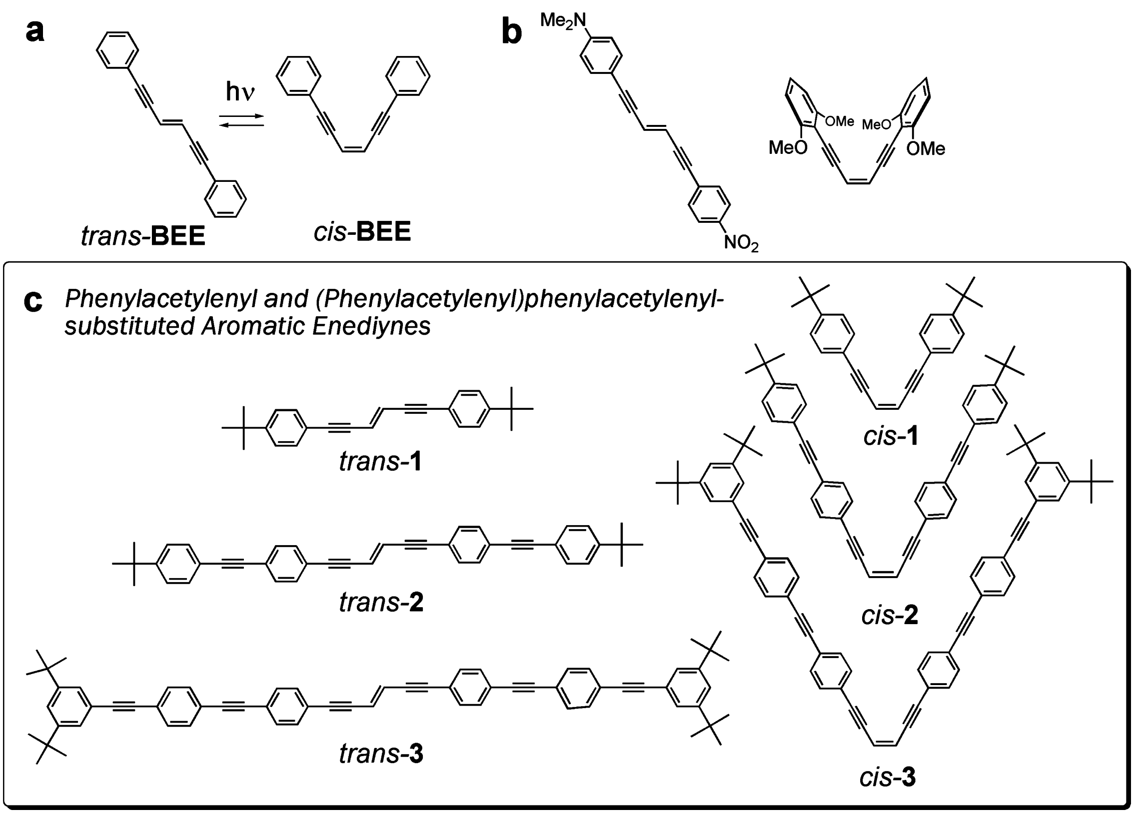

Figure 1. Chemical structures of aromatic enediynes.

unit (PicoQuant, PDL 800-B) with a repetition rate of 2.5 MHz. Temporal profiles of fluorescence decay were recorded using a microchannel plate photomultiplier (Hamamatsu, R3809U) equipped with a TCSPC computer board module (Becker and Hickl, SPC630). The full width at half-maximum (fwhm) of the instrument response function was 51 ps. Criteria for the best fit included χ^2 values and Durbin−Watson parameters obtained by nonlinear regression.[12]

Materials. ***cis-1,6-Bis(4-tert-butylphenyl)hexa-3-en-1,5-diyne (cis-1).*** A solution of *cis*-1,2-dichloroethylene (456 mg, 4.71 mmol) and 1-*tert*-butyl-4-ethynylbenzene (2.43 g, 15.4 mmol) in benzene was added to a mixture of $Pd(PPh_3)_4$ (336 mg, 29 μmol), CuI (109 mg, 0.57 mmol), and *n*-$BuNH_2$ (1.15 g, 15.7 mmol) in 20 mL of deaerated benzene which was cooled at −78 °C. The mixture was allowed to warm to room temperature and was stirred for 14 h. The reaction was then quenched by addition of water and extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by silica gel column chromatography (eluent, hexane/chloroform (80/20)) to give *cis*-**1** as a pale yellow solid (1.08 g, 59%). ^{1}H NMR (270 MHz, $CDCl_3$): 7.46 (d, J = 8.1 Hz, 4H), 7.35 (d, J = 8.1 Hz, 4H), 6.02 (s, 2H), 1.32 (s, 9H). ^{13}C NMR (270 MHz, $CDCl_3$): 31.2, 34.9, 86.8, 97.7, 119.1, 120.1, 125.3, 131.2, 151.7. Anal. Calcd for $C_{26}H_{28}$: C, 91.71; H, 8.29. Found: C, 91.57; H, 8.29.

trans-1,6-Bis(4-tert-butylphenyl)hexa-3-en-1,5-diyne (trans-1). A benzene solution of *trans*-1,2-dichloroethylene (300 mg, 3.0 mmol) and 1-*tert*-butyl-4-ethynylbenzene (1.2 g, 7.0 mmol) was added to a mixture of $Pd(PPh_3)_4$ (420 mg, 0.36 mmol), CuI (95 mg, 0.50 mmol), and *n*-$BuNH_2$ (650 mg, 9.0 mmol) in 30 mL of deaerated benzene which was cooled at −78 °C. The mixture was allowed to warm to room temperature and then stirred for 14 h, after which time the reaction was quenched by addition of water and then extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by silica gel column chromatography (eluent, hexane/chloroform (90/10)) to give *trans*-**1** as a white powder (67 mg, 5%). ^{1}H NMR (270 MHz, $CDCl_3$): 7.41−7.32 (m, 8H), 6.26 (s, 2H), 1.33 (s, 18H). ^{13}C NMR (67.5 MHz, $CDCl_3$): 31.2, 34.9, 87.6, 94.9, 120.0, 120.4, 125.3, 131.2, 151.8. Anal. Calcd for $C_{26}H_{28}$: C, 91.71; H, 8.29. Found: C, 91.94; H, 8.35.

cis-1,6-Bis(4-(2-(4-tert-butylphenyl)ethynyl)phenyl)hexa-3-en-1,5-diyne (cis-2). A benzene solution of *cis*-1,2-dichloroethylene (97 mg, 1.0 mmol) and 1-(2-(4-*tert*-butylphenyl)ethynyl)-4-ethynylbenzene[13] (580 mg, 2.2 mmol) was added to a mixture of $Pd(PPh_3)_4$ (56 mg, 0.05 mmol), CuI (27 mg, 0.14 mmol), and *n*-$BuNH_2$ (217 mg, 3.0 mmol) in 20 mL of deaerated benzene which was cooled at −78 °C. The mixture was allowed to warm to room temperature and then stirred for 14 h, after which time the reaction was quenched by addition of water and extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by silica gel column chromatography (eluent, hexane/chloroform (80/20)) to give *cis*-**2** as a white powder (110 mg, 20%). ^{1}H NMR (270 MHz $CDCl_3$): 7.48−7.45 (m, 12H), 7.39−7.36 (m, 4H), 6.12 (s, 2H), 1.33 (s, 18H). ^{13}C NMR (67.5 MHz, $CDCl_3$): 31.2, 34.9, 88.4, 89.0, 91.8, 97.6, 119.5, 119.8, 122.5, 123.8, 125.3, 131.3, 131.5, 131.5, 151.7. Anal. Calcd for $C_{42}H_{36}$: C, 92.98; H, 6.78. Found: C, 93.29; H, 6.71.

trans-1,6-Bis(4-(2-(4-tert-butylphenyl)ethynyl)phenyl)hexa-3-en-1,5-diyne (trans-2). A solution of *cis*-**2** (50.0 mg, 0.09 mmol) in 20 mL of chloroform was exposed to a hand-held UV lamp (365 nm) for 12 h. After evaporation, the residue was purified by GPC on a TSKgel G1000H column (TOHSO) by elution with hexane to give *trans*-**2** as a white powder (9.4 mg, 19%). ^{1}H NMR (270 MHz,$CDCl_3$): 7.49 (d, J = 8.1 Hz, 4H), 7.47 (d, J = 8.1 Hz, 4H), 7.43 (d, J = 8.1 Hz, 4H), 7.38 (d, J

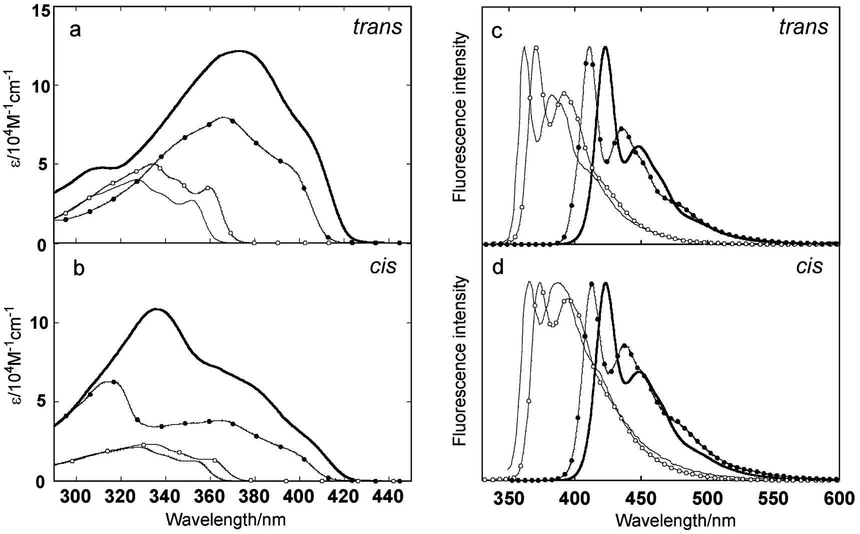

Figure 2. Absorption spectra of the (a) trans and (b) cis isomers of **BEE** (thin line), **1** (open circles), **2** (closed circles), and **3** (solid line) in benzene under argon. Fluorescence spectra of the (c) trans and (d) cis isomers of **BEE** (thin line), **1** (open circles), **2** (closed circles), and **3** (solid line) in benzene under argon.

= 8.1 Hz, 4H), 6.30 (s, 2H), 1.33 (s, 18H). MALDI-TOFMS (*m*/*z*) $[M]^+$ calcd for $C_{42}H_{36}$, 540.28; found, 540.01.

***cis*-1,6-Bis(4-(2-(4-(2-(3,5-di-*tert*-butylphenyl)ethynyl)phenyl)ethynyl)phenyl)hexa-3-en-1,5-diyne (*cis*-3).** A benzene solution of *cis*-1,2-dichloroethylene (20 mg, 0.2 mmol) and 1,3-di-*tert*-butyl-5-(2-(4-(2-(4-ethynylphenyl)ethynyl)phenyl)-ethynyl)benzene[13] (203 mg, 0.49 mmol) was added to a mixture of $Pd(PPh_3)_2Cl_2$ (23 mg, 0.03 mmol), CuI (9.1 mg, 0.04 mmol), and *n*-$BuNH_2$ (50 mg, 0.68 mmol) in 10 mL of deaerated benzene which was cooled at −78 °C. The mixture was allowed to warm to room temperature and stirred for 5 h. After evaporation, the residue was purified by silica gel column chromatography (eluent, hexane/chloroform (85/15)) to give *cis*-**3** as a white powder (28 mg, 16%). ^1H NMR (400 MHz,$CDCl_3$): 7.54−7.46 (m, 16H), 7.41−7.40 (m, 2H), 7.38−7.37 (m, 4H), 6.12 (s, 2H), 1.33 (s, 36H). ^{13}C NMR (67.5 MHz, $CDCl_3$): 150.8, 131.5, 131.5, 131.5, 131.4, 125.8, 123.6, 122.9, 122.9, 122.4, 121.8, 119.6, 97.5, 92.6, 91.4, 90.7, 89.2, 87.8, 34.9, 31.4. MALDI-TOFMS (*m*/*z*) $[M + H]^+$ calcd for $C_{66}H_{60}$, 853.47; found, 853.47.

***trans*-1,6-Bis(4-(2-(4-(2-(3,5-di-*tert*-butylphenyl)ethynyl)phenyl)ethynyl)phenyl)hexa-3-en-1,5-diyne (*trans*-3).** A benzene solution of *trans*-1,2-dichloroethylene (20 mg, 0.2 mmol) and 1,3-di-*tert*-butyl-5-(2-(4-(2-(4-ethynylphenyl)ethynyl)phenyl)-ethynyl)benzene (22 mg, 0.53 mmol) was added to a mixture of $Pd(PPh_3)_2Cl_2$ (22 mg, 0.03 mmol), CuI (7.8 mg, 0.04 mmol), and *n*-$BuNH_2$ (53 mg, 0.72 mmol) in 10 mL of deaerated benzene which was cooled at −78 °C. The mixture was allowed to warm to room temperature and stirred for 6 h. After evaporation, the residue was purified by silica gel column chromatography (eluent, hexane/chloroform (90/10)) to give *trans*-**3** as a white powder (18.4 mg, 10.8%). ^1H NMR (270 MHz, $CDCl_3$): 7.55−7.45 (m, 16H), 7.42−7.39 (m, 6H), 6.31 (s, 1H), 1.34 (s, 36H). ^{13}C NMR (67.5 MHz, $CDCl_3$): 150.8, 131.5, 131.5, 131.4, 125.8, 123.6, 123.3, 123.0, 122.6, 122.4, 121.8, 120.8, 94.9, 92.6, 91.4, 90.3, 90.0, 87.8, 34.9, 31.4. MALDI-TOFMS (*m*/*z*) $[M + H]^+$ calcd for $C_{66}H_{60}$, 853.47; found, 853.48.

Results and Discussion

Steady State Absorption and Fluorescence Spectra. The para-substituent effect of the phenylacetylenyl group is significant. The UV absorption spectrum of *trans*-**BEE** in benzene is reported to exhibit an absorption band around 300−360 nm.[5] The absorption spectra of both *trans*-**BEE** and the *tert*-butyl substituted analogue *trans*-**1** and phenylacetylenyl and (phenylacetylenyl)phenylacetylenyl substituted enediynes *trans*-**2** and *trans*-**3** in benzene solution are shown in Figure 2a. The spectra of *trans*-**1** is slightly red-shifted compared to that of *trans*-**BEE**, presumably due to the difference in electron-donating ability of H and the *tert*-butyl group. Compared with the absorption spectrum of *trans*-**1**, the spectrum of *trans*-**2** is dramatically red-shifted to 420 nm and its shape is also changed, indicating that the π-electrons of the para-substituted phenylacetylenyl group are delocalized into the core enediyne moiety. There is also a shoulder at 395 nm in the spectrum for *trans*-**2** that seems to correspond to shoulders at 352 nm in the spectrum for **BEE** and 360 nm in the spectrum for *trans*-**1**. Interestingly, the absorption spectrum of *trans*-**3** showed only slight red-shifting compared to that of *trans*-**2** despite further extension of the π-conjugate system, while the extinction coefficient increased significantly to as high as 122000 M^{-1} cm^{-1}.

Some similarities and differences were also noted for the corresponding cis isomers. Their absorption spectra can be seen in Figure 1b. Although the extinction coefficients of the cis isomers are almost half as much as the values for the trans isomers, the spectral shape of *cis*- and *trans*-**1** are quite similar to each other. The shapes of the spectra for *cis*-**2** and *cis*-**3**, however, are different from those of the corresponding trans isomers. The absorption band of *cis*-**2** consists of the superposition of a broad band around 330−420 nm similar to that seen in *trans*-**1** and a band peaking at 315 nm, probably arising from partial localization of the π-electron system at the phenylacetylene moiety in the cis isomer. A similar trend was observed in *cis*-**3**; the absorption band consists of two independent parts, a broad band around 350−420 nm and a strong band peaking at 336 nm, which may be ascribed to the band of the origo(phenylacetylene) unit.[14−16] The energies for the lowest transition were calculated to be 81, 79, 71, and 70 kcal/mol for both trans and cis isomers of **BEE**, **1**, **2**, and **3**, respectively.

The phenylacetylene substituents also have an impact on the fluorescence spectra, which are shown for the trans and cis isomers in parts c and d of Figure 2, respectively, with some relevant data also presented in Table 1. *trans*-**BEE** is reported

TABLE 1: Spectroscopic, Photophysical, and Photochemical Data (Benzene Solution, 298 K)

	λ_{max} (abs) /nm	ϵ_{max}/M^{-1} cm^{-1}	λ_{max} (fl)/nm	Stokes shift/cm^{-1}	lowest singlet energy/kcal mol^{-1}	Φ_f	τ_S/ns	$\Phi_{t\to c}$	$\Phi_{c\to t}$	τ_T/ns	$K_q/10^9$ M^{-1} s^{-1}
trans-**BEE**	328, 352	40100, 27100	362, 382	780	81	0.42		0.17		0.37	
trans-**1**	334, 360	52200, 35200	370, 392	750	79	0.61	0.69	0.10		0.49	4.22
trans-**2**	365, 395	79700, 50000	411, 436	990	71	0.61	0.61	0.007		2.45	3.25
trans-**3**	373, 405	122000, 66000	423, 448	1050	70	0.47	0.52	0.004		2.86	2.88
cis-**BEE**	328, 352	21100, 12600	364, 387	940	81	0.31	0.88		0.27	0.37	
cis-**1**	333, 359	23300, 13900	373, 394	1050	79	0.39	1.13		0.19	0.48	4.16
cis-**2**	315, 365, 395	62700, 38200, 19500	413, 437	1100	71	0.60	1.42		0.03	2.47	2.94
cis-**3**	336, 375, 405	108800, 63000, 25000	423, 448	1050	70	0.42	1.28		0.02	2.86	3.04

to exhibit a fluorescence band with $\lambda_{max} = 362$ and 381 nm and $\Phi_f = 0.42$ in benzene under argon.[5] The fluorescence of *trans*-**1** is similar to that of *trans*-**BEE** but more intense ($\Phi_f = 0.61$). The fluorescence spectrum of *trans*-**2** is more than 40 nm red-shifted to 411 and 436 nm and exhibits a long tail at low energy around 560 nm. The fluorescence quantum yield of *trans*-**2** ($\Phi_f = 0.61$) is the same value as *trans*-**1**, and the singlet lifetime is similar: $\tau_s = 0.69$ ns for *trans*-**1** and 0.61 ns for *trans*-**2**, respectively. The fluorescence spectrum of *trans*-**3** is slightly (11 nm) red-shifted compared to that of *trans*-**2** and exhibits a long tail at low energy around 560 nm which is almost the same as that of *trans*-**2**. The fluorescence quantum yield of *trans*-**3** ($\Phi_f = 0.48$) is lower than those of *trans*-**1** and *trans*-**2**, and the singlet lifetime is shorter (0.47 ns), probably due to the promotion of nonradiative decay processes.

The Stokes shift values (780, 990, and 1050 cm^{-1} for *trans*-**1**, *trans*-**2**, and *trans*-**3**, respectively) only slightly increase with expansion of the phenylacetylene chain, indicating that the structural differences between the ground state and the excited singlet state are not very significant among **1**−**3**. In the ground state, both planar and perpendicular conformations at the phenylacetylene moiety should exist because of free rotation of the single bonds, whereas in the excited singlet state an immediate structural change to the planar conformation takes place that results in fluorescence.[17,18] In this case, the enediyne having a longer phenylacetylene chain could cause more significant conformational changes in the excited singlet state,[15] resulting in a greater value of the Stokes shift than that observed for the shorter chain. However, the calculated values of the Stokes shift using the lowest energy transition band of the absorption spectra is not very much different, suggesting that the conformation of the fluorescent state should be almost similar among **1**−**3**.

Fluorescence lifetimes of the examined molecules are also listed in Table 1. All compounds exhibited single exponential decay, and the wavelength dependence of time constants was not observed, indicating a single emitting state in all cases.

Excitation Spectra. Excitation spectra provided further information about the substituted endiynes. Figure 3 shows fluorescence excitation and absorption spectra. All of the trans isomers and *cis*-**1** exhibited similar absorption and excitation spectral shapes, whereas the excitation spectra of *cis*-**2** and *cis*-**3** did not agree with their absorption spectra, especially at the shorter wavelength region. This result indicates that interaction between the phenylacetylenyl units and the enediyne chromophore is not significant in *cis*-**2** and *cis*-**3**. In addition, the energy transfer from excited phenylacetylenyl units to the enediyne chromophore does not occur efficiently, despite the fact that the phenylacetylenyl units are substituted in the para position. In other words, the excitation at 315 and 336 nm for *cis*-**2** and *cis*-**3**, respectively, can produce locally excited states at the phenylacetylenyl units that mainly decay nonradiatively.[19−21] On the other hand, distinctive absorption bands for phenylacetylenyl units cannot be observed in the spectra for *trans*-**2** and *trans*-**3**, indicating that the π-electron system delocalizes over the whole molecule in these isomers.

Photoisomerization. Aromatic enediynes are known to undergo a variety of photochemical processes including trans−cis photoisomerization. The changes in the absorption spectra observed upon irradiation with 365 nm light in benzene solution under argon are shown in Figure 4, and some relevant data are gathered in Table 1. Since the isosbestic point can be observed during the photoirradiation (for **2** and **3** only) and the spectral shapes at the photostationary state of the trans-starting and cis-starting sample (solid line) are almost identical, the trans−cis photoisomerization in the examined molecules is a clean process

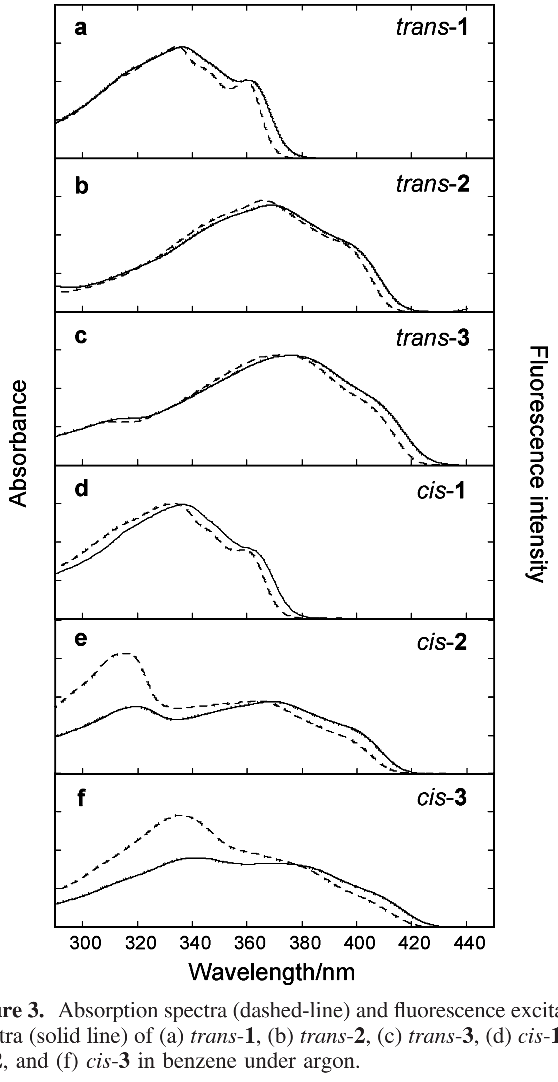

Figure 3. Absorption spectra (dashed-line) and fluorescence excitation spectra (solid line) of (a) *trans*-**1**, (b) *trans*-**2**, (c) *trans*-**3**, (d) *cis*-**1**, (e) *cis*-**2**, and (f) *cis*-**3** in benzene under argon.

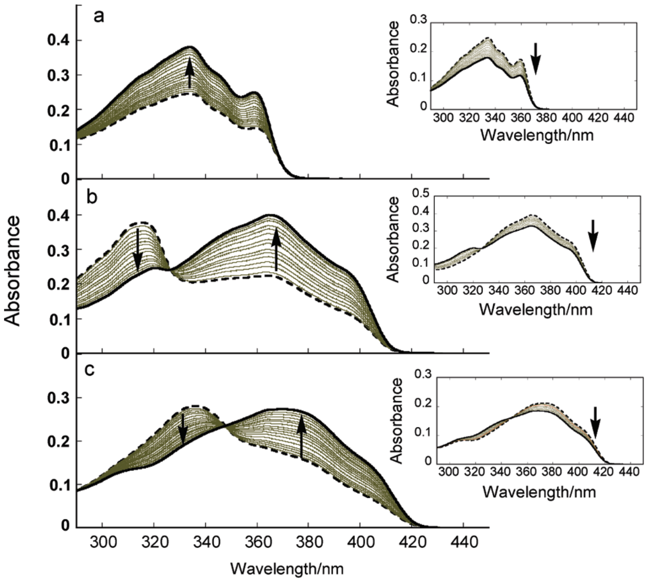

Figure 4. Change in the absorption spectra of (a) *cis*-**1**, (b) *cis*-**2**, and (c) *cis*-**3** upon irradiation with 365 nm light in benzene under argon. Inset shows change in the absorption spectra of the corresponding trans isomer upon irradiation with 365 nm light under the same conditions.

and the photoproducts are either the trans or cis isomers. The lack of observation of isosbestic point for **BEE** and **1** is due to the similarity of the absorption spectra of trans and cis isomers with smaller extinction coefficient around 300−350 nm in cis isomer. From the absorption spectra of pure trans and cis isomers, the trans/cis ratio at the photostationary state ([trans]/[cis])$_{pss}$ can be calculated to be 48/52, 70/30, and 73/27 for **1**, **2**, and **3**, respectively. This indicates that the photoismerization from trans isomer is more difficult than that from cis isomer in **2** and **3**. The quantum yields for trans-to-cis photoisomerization ($\Phi_{t\to c}$) of *trans*-**1** are calculated by the equation

$$\Phi_{t\to c} = \Phi_{c\to t}\varepsilon_{cis}/\varepsilon_{trans}x([\mathrm{trans}]/[\mathrm{cis}])_{pss} \qquad (1)$$

where ε_{cis} and ε_{trans} are the molar extinction coefficients at 365 nm for *cis*-**1** and *trans*-**1**, respectively, and $\Phi_{c\to t}$ is the quantum yield for cis-to-trans photoisomerization obtained at a very early stage.

The $\Phi_{t\to c}$ value obtained for *trans*-**1** (0.10) is on the same order as that obtained for *trans*-**BEE** (0.19), whereas those for *trans*-**2** (0.007) and *trans*-**3** (0.004) are considerably smaller. The much lower $\Phi_{t\to c}$ values for *trans*-**2** and *trans*-**3** may be due in part to steric interactions with surrounding solvent molecules during rotation around the C=C double bond of the phenylacetylene enediyne. It is more likely, though, to be related to the promotion of alternative nonradiative decay processes due to the lower excited state energy of *trans*-**2** and *trans*-**3** or the presence of an increasing number of possible reaction pathways from the emitting species to a nonemitting perpendicular species in the excited state.[19] Photoisomerization could thus proceed mainly via the excited triplet state (see below). The quantum yield for nonradiative decay other than photoisomerization (Φ_{nr}) can be calculated using the Φ_f and $\Phi_{t\to c}$ values

$$\Phi_{nr} = 1 - (\Phi_f + \Phi_{t\to c}) \qquad (2)$$

The calculated Φ_{nr} values are 0.19, 0.38, and 0.52 for *trans*-**1**, *trans*-**2**, and *trans*-**3**, respectively. Similar values were obtained for the cis isomers. These values support above statements that nonradiative decay processes are promoted with increasing chain length.

Transient Absorption Spectra. Transient absorption spectra were collected to gain further insight into the excited states of compounds **1**−**3**. Upon 355 nm laser excitation, each one of the trans and cis isomers gave a clear transient absorption spectrum (Figure 5). The observed transient species for all compounds were quenched by oxygen with a rate constant of (2.9−4.2) × 10^9 M^{-1} s^{-1} (Table 1), indicating that the observed transients are assignable to the triplet state.[22] The transient absorption spectra of the trans and cis isomers are quite similar to each other (Figure 5). In addition, the triplet lifetimes (τ_t) are almost the same for the trans and cis isomers (Table 1), suggesting that both undergo intersystem crossing to the triplet state where the planar triplet state (^{3}trans* and ^{3}cis*) and the perpendicular triplet state (^{3}p*) are equilibrated. The potential energy of ^{3}p* does not change with introduction of substituents on the phenyl ring,[22] and thus the energies of ^{3}p* are nearly the same among all examined compounds (Figure 6), whereas the energies of the planar conformations ^{3}trans* and ^{3}cis* depend on the substituent. The energies of ^{3}trans* and ^{3}cis* of **1** and **BEE** are nearly the same based on the similarities in their T−T absorption spectra. The energies of ^{3}trans* and ^{3}cis* of **2** and **3**, however, are expected to be lower than those of **1** based on the fact that the triplet lifetimes of **2** and **3** are 5−6 times longer than that of **1**. The lower planar triplet energies in **2** and **3** probably promote a nonradiative deactivation process from the planar triplet state (Figure 6), and therefore the quantum yield of isomerization is much lower in **2** and **3** than it is in **BEE** and **1**. This result indicates that the photoisomerization of **1**−**3** partially proceeds from the excited triplet state.

Since the deactivation rate constant from ^{3}trans* to the ground state trans isomer is reasonably estimated to be the same as that from ^{3}cis* to the ground state cis isomer, the equilibrium constant between the planar triplet state (^{3}trans* and ^{3}cis*) and ^{3}p* can be estimated using the observed triplet lifetime. The triplet lifetime (τ_t) can be described in the equation

$$\tau_t = (1 + K)/(Kk_d + k_d') \qquad (3)$$

where k_d and k_d' are the rate constants for deactivation from the planar triplet state and ^{3}p*, respectively, and K is the equilibrium constant between the planar triplet state and ^{3}p*. The k_d and k_d' values were previously estimated to be 2 × 10^4 s^{-1} and 2 × 10^7 s^{-1}, respectively.[22] Using this information, the equilibrium constants K were determined to be 0.11, 0.020, and 0.020 for **1**, **2**, and **3**, respectively (Table 2). Furthermore, the proportion of the planar and perpendicular excited triplet species (^{3}trans* and ^{3}cis*) and ^{3}p* was roughly estimated to be 89:11, 98:2, and 98:2 for **1**, **2**, and **3**, respectively (Table 2). These values support that the energies of planar triplet state in **2** and **3** are lower than that of **1** and the quantum yield of isomerization is much lower in **2** and **3** due to the promotion of a nonradiateve process from the planar triplet state.

Potential Energy Surfaces. On the basis of the experimental results, the potential energy surfaces of **1**−**3** were estimated and are depicted in Figure 6. The potential energy surfaces for photoisomerization depend on the length of the phenyl acetylenyl chain. In the triplet state, the three conformers ^{3}trans* and ^{3}cis* and ^{3}p* are equilibrated and the photoisomerization may take place from the ^{3}p* conformer. In particular, the energies

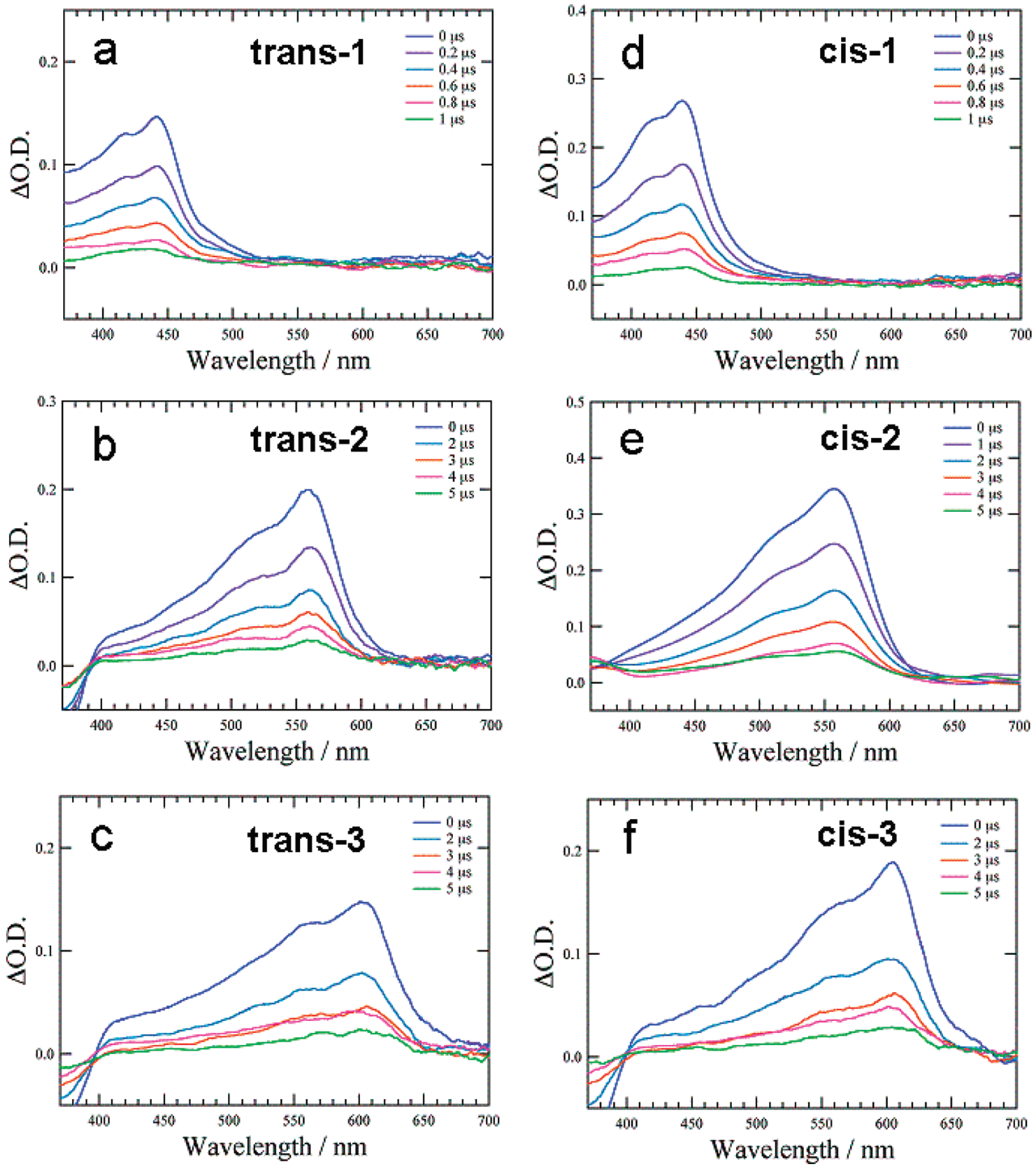

Figure 5. Transient absorption spectra of (a) *trans*-**1**, (b) *trans*-**2**, (c) *trans*-**3**, (d) *cis*-**1**, (e) *cis*-**2**, and (f) *cis*-**3** in benzene under argon.

of the planar conformations of **2** and **3** are lower than that of **1**, while those of ^{3}p* are independent of the length of the phenyl acetylenyl chain. The result is a higher activation energy for excitation from the planar conformations to ^{3}p* in **2** and **3** and thus a decrease in the quantum yield of the photoisomerization process. In addition, deactivation processes related to the phenylacetylene group may also be a source of nonradiative decay.[19]

Conclusion

In summary, a series of phenylacetylenyl- and (phenylacetylenyl)phenylacetylenyl-substituted aromatic enediynes **1**−**3** were synthesized as pure trans and cis isomers and their photochemical properties studied. With expansion of the π-electron system, the absorption spectra red-shifted and the molar extinction coefficients dramatically increased in both the trans and cis isomers. The absorption spectra of *cis*-**2** and *cis*-**3** consist of two distinctive absorption bands of which the band at the shorter wavelength region is ascribed to the substituted phenylacetylenyl units. The fluorescence excitation spectra of both *cis*-**2** and *cis*-**3** do not agree with those of the absorption spectra, indicating

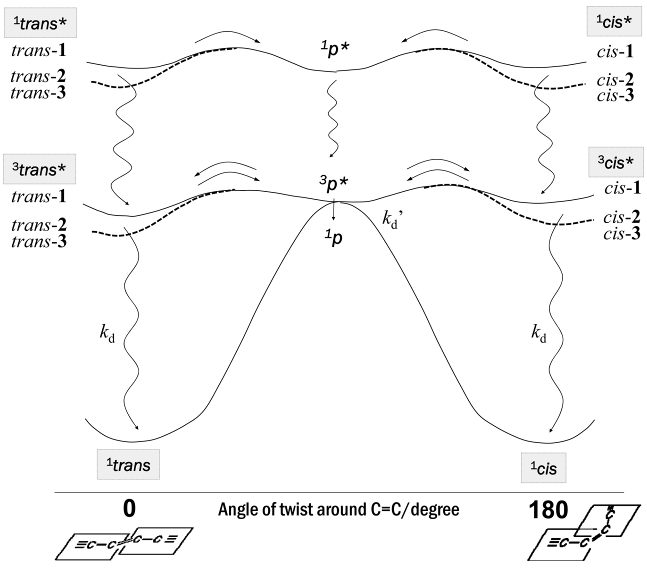

Figure 6. Potential energy surfaces for the photoisomerization of **1**−**3**.

TABLE 2: Equilibrium Constants between the Planar (^{3}trans* and ^{3}cis*) and Perpendicular Triplet States (^{3}p*) and the Population Ratio of the Planar and Perpendicular Triplet States in Benzene under Argon

	K	$\{[^3p^*]/[^3\text{trans}^*] + [^3\text{cis}^*]\}$
BEE	0.16	16/84
1	0.11	11/89
2	0.020	2/98
3	0.020	2/98

that the excited state of phenylacetylenyl units in *cis*-**2** and *cis*-**3** mainly decay nonradiatively. The fluorescence quantum yields of examined molecules were high, even for the cis isomers ($\Phi_f = 0.39-0.61$). The fluorescence decay of each one of the compounds was analyzed as a single exponential and the wavelength dependence of time constants was not observed, indicating the presence of a single emitting state in all cases. All isomers exhibited mutual cis−trans photoisomerization. The quantum yield of both trans-to-cis and cis-to-trans photoisomerization considerably decreased in **2** and **3**, presumably because of an increase in the number of photochemical processes that yield nonfluorescent excited species. Furthermore, three energy minima exist in the excited triplet state where the energy of the planar conformation decreased with extension of the phenyl acetylenyl chain, resulting in the promotion of nonradiative processes without conformational change.

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