Photochemical and Photophysical Characteristics in the Excited State Properties of Methoxy-substituted Enediynes

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Effects of methoxy substituent on the phenyl ring of cis isomer of enediynes were explored. All the cis isomers exhibited fluorescence emission with moderate efficiency. Furthermore, the ortho-substituted compounds showed red shift of the fluorescence emission even though crystallographic analysis suggests that the single bond connecting the phenyl ring and carbon–carbon triple bond takes considerably twisted conformation.

Stilbenoid compounds and azobenzenes are known to isomerize mutually between trans and cis isomers by photo-irradiation.[1–4] Although the *trans*-stilbene gives fluorescence with the quantum yield of 0.04 in hexane at room temperature, *cis*-stilbene and both *cis*- and *trans*-azobenzene do not exhibit fluorescence at room temperature owing to the existence of the fast deactivation processes from the singlet excited state to give the corresponding isomers or photocyclization product.

In contrast, not only trans isomer but also cis isomer of aromatic enediyne is highly fluorescent. Thus, they deactivate through fluorecence emission, cis–trans photoisomerization, or intersystem crossing processes from the excited singlet state.[5,6] Since the introduction of methoxy substituent at the phenyl ring of stilbene increased the fluorescence quantum yield and the fluorescence lifetime,[7–9] we have investigated the effect of methoxy substituent on the excited state properties of enediyne compounds.

The methoxy-substituted aromatic enediynes on 2,2′,6,6′ (*o*-MEY), 3,3′,5,5′ (*m*-MEY), and 4,4′ positions (*p*-MEY) of the phenyl ring were newly synthesized (Figure 1) and identified by NMR and elemental analysis.[10]

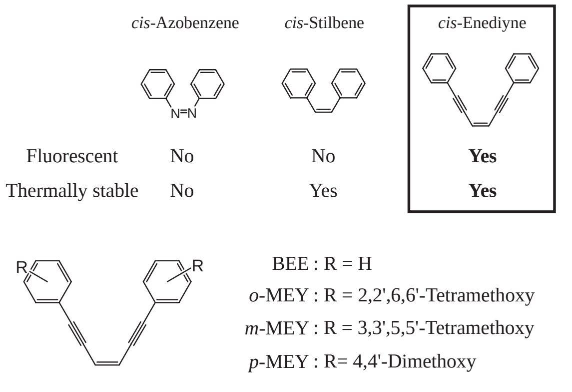

Figure 1. Chemical structures of cis aromatic enediynes.

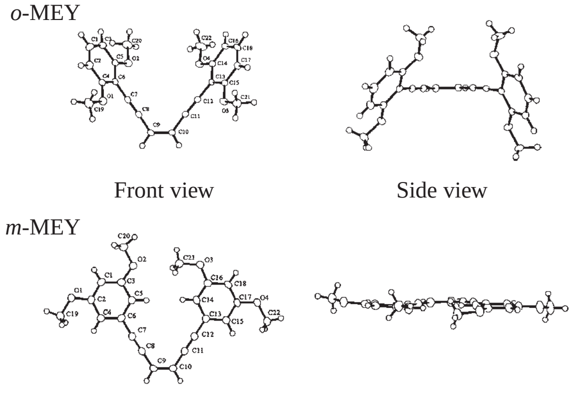

Figure 2. X-ray crystal structures of *o*-MEY (top) and *m*-MEY (bottom).

Substitution of the methoxy group at the ortho positions should strongly affect the ground state structure of cis aromatic enediyne. Figure 2 shows ORTEP diagrams of *o*-MEY and *m*-MEY. While the terminal phenyl rings of *m*-MEY takes a coplanar structure, those of *o*-MEY takes a nonplanar structure due to the steric hindrance caused by two methoxy groups at ortho positions.[11] The dihedral angle between the phenyl ring and the enediyne part is calculated to be more than 55° (Table S2 in Supporting Information).[10]

Figure 3 shows the absorption and fluorescence spectra of *cis*-enediyne in benzene at room temperature. The introduction

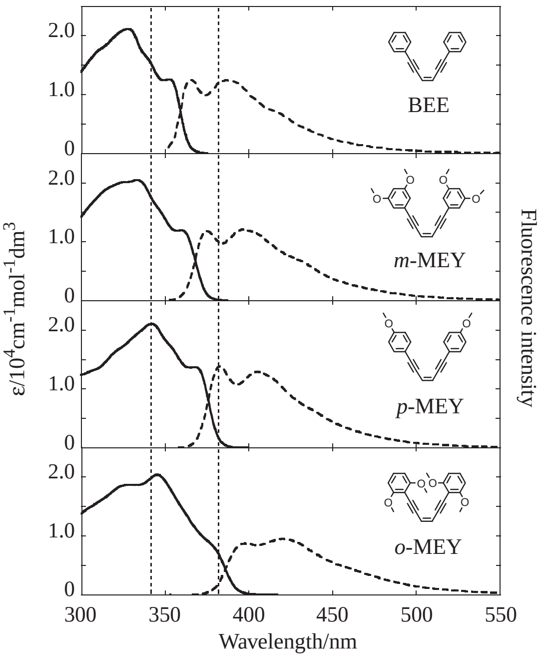

Figure 3. Absorption (solid lines) and fluorescence (dashed lines) spectra of BEE, *m*-, *p*-, and *o*-MEY in benzene under Ar.

Table 1. Spectroscopic parameters of *o*-, *m*-, *p*-MEY, and BEE

Substrate	$\lambda_{\max}$ (abs) /nm	$\varepsilon_{\max}$ /$\mathrm{cm^{-1}\,mol^{-1}\,dm^{3}}$	$\lambda_{\max}$ (fl) /nm	Stokes shift /$\mathrm{cm^{-1}}$	Φ_f	Φ_{isc}	$\Phi_{c\to t}$	$(\Phi_{c\to t}{}^{S}, \Phi_{c\to t}{}^{T})$	τ_s/ns	τ_T/ns	E_S /kcal mol^{-1}
o-MEY	346, 376	20400, 9700	399, 421	1506	0.35	0.35	0.30	(0.12, 0.18)	1.25	980	73.9
m-MEY	334, 357	20500, 11900	375, 396	1143	0.22	0.25	0.16	(0.04, 0.12)	0.91	530	78.2
p-MEY	343, 369	21100, 13700	382, 404	1023	0.48	0.23	0.27	(0.15, 0.12)	1.32	520	76.2
BEE	328, 352	21100, 13300	364, 387	937	0.31	0.25	0.27	(0.14, 0.13)	—	370	79.6

of the methoxy group resulted in the red-shift in the absorption and fluorescence spectra of *o*-MEY, *m*-MEY, and *p*-MEY compared to the parent endiyne compound BEE. While the spectra of *m*-MEY and *p*-MEY showed similar vibronic features to BEE, the spectra of *o*-MEY showed broadened vibronic features probably because of the twisting of the single bond connecting the phenyl ring and carbon–carbon triple bond.

All *cis*-enediynes showed fluorescence emission with relatively high quantum efficiency (Φ_f) of 0.35, 0.22, and 0.48 for *o*-MEY, *m*-MEY, and *p*-MEY, respectively (Table 1). The lifetimes of the excited singlet state for *o*-MEY, *m*-MEY, and *p*-MEY were determined to be 1.25, 0.91, and 1.32 ns, respectively. These lifetimes were much longer than that of *cis*-stilbene (less than 2 ps) in agreement with the strong fluorescence emission from BEE.[2] The energy of the excited singlet state was estimated from the crossing point of the absorption spectra and fluorescence spectra to be 73.9, 78.2, and 76.2 kcal mol^{-1}, for *o*-MEY, *m*-MEY, and *p*-MEY, respectively. The energy increased in the order of *o*-, *p*-, and *m*-MEY, and these values are lower than that of BEE (79.6 kcal mol^{-1}). Although *o*-MEY takes a nonplanar conformation as revealed by the dihedral angle between the phenyl ring and the enediyne part to be more than 55°, the excited singlet energy is the lowest in *o*-MEY.[10] These results suggest that the conjugation among $C{=}C$ and $C{=}C$ may be extended or almost the same even by the twisting of the single bond connecting these two chromophores.

On irradiation in benzene, all derivatives underwent cis–trans isomerization to give the photostationary state isomer ratio $([\mathrm{cis}]/[\mathrm{trans}])_{\mathrm{pss}}$ to be 76/24, 40/60, 52/48, and 44/56 for *o*-MEY, *m*-MEY, *p*-MEY, and BEE, respectively.

On 308 nm laser excitation, all derivatives gave transient absorption spectra decaying with single-exponential function (Table 1). The observed transients were quenched by oxygen with the diffusion-controlled reaction and are assigned to the triplet excited state. The quantum efficiency (Φ_{isc}) of intersystem crossing to give the excited triplet state was estimated to be 0.35, 0.25, and 0.23 for *o*-MEY, *m*-MEY, and *p*-MEY, respectively. The lifetimes of the excited triplet state were determined to be 980, 530, and 520 ns for *o*-MEY, *m*-MEY, and *p*-MEY, respectively, and longer than that of BEE. Thus, the methoxy substitution increased the triplet lifetime probably shifting the equilibrium between the planar triplet and the perpendicular triplet to the planar triplet side. One can estimate the efficiency of cis-to-trans isomerization from the triplet excited state ($\Phi_{c\to t}{}^{T}$) by following equation:

$$\Phi_{c\to t}{}^{T} = 1/2 \times \Phi_{isc}, \tag{1}$$

$$\Phi_{c\to t} = \Phi_{c\to t}{}^{S} + \Phi_{c\to t}{}^{T}, \tag{2}$$

$$\Phi_{iso} = 2 \times \Phi_{c\to t}, \tag{3}$$

where $\Phi_{c\to t}$ is the efficiency of cis-to-trans photoisomerization, $\Phi_{c\to t}{}^{S}$ is that of cis-to-trans photoisomerization only from the singlet excited state, and Φ_{iso} is that of all photoisomerization processes. These results suggest that $[\Phi_f + \Phi_{iso}]$ of *o*-MEY and *p*-MEY was 0.95 and 1.02, and was about 1 within experimental uncertainty, indicating that deactivation by nonradiative process other than intersystem crossing and isomerization process hardly occur. However, that of *m*-MEY was 0.54, indicating that large contribution of nonradiative process exists on the deactivation from the excited singlet state.

In summary, all *cis*-enediynes showed fluorescence emission with relatively high quantum efficiency. They underwent cis–trans photoisomerization and intersystem crossing. The maximum wavelengths in the absorption and fluorescence spectra and the triplet lifetime were the longest, and the quantum yield of fluorescence emission was the highest in *o*-MEY.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

11 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-659191 and 659192. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

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