Photochemical Cleavage of the Axial Group Attached to the Central Carbon Atom of Triazatriangulene

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Photocleavage reaction of triazatriangulene (TATA) leuco derivatives bearing axial substituents proceeded quantitatively in polar solvents with quantum yields (Φ_r) of up to 0.56. The photoreaction can easily be detected by the red color and yellow fluorescence originating from the photogenerated TATA cation. Electron-withdrawing groups on the axial substituent effectively suppress the photoreaction, in a particular case, Φ_r became less than 0.01.

Triphenylmethanes (TPMs) have attracted interest for a long time because of their brilliant colors and photophysical properties, which can be applicable to organic dyes and stains for tissues.^{1–5} Indeed, this skeleton has been used for many applications, including organic dyes like Crystal Violet, fluorescent chromophores like fluorescein, and pH indicators like phenolphthalein (Figure 1). Owing to the π -conjugation of TPMs, not only the parent form but also all of its radical, cation, and anion forms are stable due to the delocalization of charge or spin to the phenyl rings.^{6,7} Photochromic dyes like Malachite Green using this skeleton also have been developed. The leucocyanide of the TPM dye undergoes photocleavage of the cyano group upon UV irradiation and recombines via a thermal back reaction.^{8–10}

Triazatriangulene (TATA) cation is a derivative of the triphenylmethyl cation, in which nitrogen atoms link the three phenyl rings together to provide a rigid and planar geometry, while phenyl rings of the triphenylmethyl cation flexibly rotate. The resonance structures involving the nitrogen atoms stabilize the carbon-centered cation.^{11–13} Because of its stable cationic planar structure, applications to the surface chemistry^{14–17} and supra-molecular chemistry^{18,19} are attracting interest. Inspired by the photochromic reaction of Malachite Green, we investigated the photoreactivity of TATA leuco derivatives that have an axial group



Figure 1. Triphenylmethane-based compounds.

attached to the central carbon atom. Unlike the photochromism of Malachite Green leucocyanide, the photoreaction of the TATA leuco derivatives was irreversible because of the stability of the photogenerated TATA cation and irreversible protonation of the carbanion of the axial group upon the photocleavage reaction (Scheme 1). It was found that the photoreaction quantum yield of TATA leuco derivatives strongly depends on the axial group. The difference in the photoreactivity was discussed in view of the substituent effect, solvent effect, and density functional theory (DFT) calculations.

The studied compounds bearing different axial groups 1-6 are shown in Figure 2. Compounds 1, 2, and 6 are known compounds.²⁰ The leuco derivatives can be easily synthesized through the nucleophilic attack of the carbanion to the center of the TATA cation (see the Supporting Information for details). The structures of 1-6 were characterized by NMR spectroscopy and mass spectrometry.

The absorption spectra of compounds **1** and **2**, and the absorption and fluorescence spectra of the TATA cation tetrafluoroborate salt (TATA⁺BF₄⁻) were measured in acetonitrile (Figure S1). The solution of TATA⁺BF₄⁻ shows a characteristic structured absorption band at 525 nm and a fluorescence band at 562 nm, and shows a red color and a yellow emission under UV irradiation.²¹ On the other hand, the solutions of the leuco derivatives **1** and **2** appeared to be colorless owing to the change of the orbital hybridization from



Scheme 1. Irreversible photocleavage of TATA leuco derivative.



Figure 2. TATA leuco derivatives bearing different axial groups at the central carbon atom.



Figure 3. Absorption spectral change of compounds (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6 in ethanol before (black solid line) and after (blue dashed line) UV irradiation (313 nm). The adsorption spectra of 5 and 6 are recorded at concentration of 2×10^{-5} M, that is lower than compounds 1–4 ($c = 5 \times 10^{-5}$ M), because of the low solubility of 5 and 6. The red dotted lines denote the spectrum of TATA⁺BF₄⁻ at the same concentration. (g) The plot of the absorbance of 2 (black square), 5 (blue triangle), and 6 (red circle) at 525 nm against the time of UV irradiation.

 sp^2 to sp^3 at the central carbon atom. This feature was clearly seen in the absorption spectra; the absorption bands of **1** and **2** were observed at only less than 370 nm. An absorption band corresponding to the axial substituent was clearly observed for compounds **4** and **5** at ca. 400 nm, and **6** at ca. 350 nm in ethanol (Figure 3).

Photocleavage reactions of 1-6 were investigated in ethanol (Figure 3). For the phenyl-substituted compound 1, two absorption bands were generated upon irradiation with UV light (313 nm): one is the structured band appearing at 525 nm, corresponding to the TATA cation and the other is a weaker band at ca. 600 nm (Figure 3a). As the absorption band at 525 nm increased, the colorless solution turned red. The shape of the absorption band at 525 nm is in good agreement with that of the TATA cation; however, the weaker band around 600 nm is absent in the spectrum of the TATA cation, suggesting generation of side products upon UV irradiation of the phenyl derivative 1. On the other hand, the ethynylene derivatives 2-4 showed cleaner photoreactions in the solvent (Figures 3b–3d). In these cases, the band at \sim 600 nm was not observed. Not only the shape but also the magnitude of the absorption band at 525 nm corresponds to the TATA cation at the same concentration, suggesting a quantitative photoreaction of 2-4. For the 9-anthrylethynyl derivative 4, the structured absorp-



Figure 4. ¹H NMR spectra of compound **2** in ethanol- d_6 (a) before and after UV irradiation (365 nm) for (b) 3, (c) 10, and (d) 20 min. Reference spectra of (e) TATA⁺BF₄⁻ and (f) phenylacetylene. Filled circle denotes the proton peaks of compound **2**, and open circle and triangle denote those of the photogenerated TATA⁺BF₄⁻ and phenylacetylene, respectively. The small difference in chemical shift upon UV irradiation may be attributed to the change in polarity of medium or intermolecular interactions caused by the concentration change of components.

tion band of the photogenerated 9-ethynylanthracenene was also observed at the wavelength range from 300 to 400 nm. It is noted that the absorption spectrum of **2** after UV irradiation did not change at least for 24 h at room temperature (Figure S2), suggesting thermal stability of the TATA⁺EtO⁻ salt.

The formation of side products was more prominent when the photoreaction was carried out in an aprotic solvent (Figure S3). Upon UV irradiation of 1 in acetonitrile, the absorption bands not only at 600 nm but also at 400 nm appeared. When acetonitrile containing 5-10 vol % of water was used for solvent, the magnitude of the band at 400 nm decreased and the band at 525 nm increased simultaneously upon irradiation. However, the band at 600 nm was not influenced by the presence of water (Figure S3a). In the case of compound 2, the appearance of the absorption bands around 300-400 nm was effectively suppressed and the quantitative production of the TATA cation was observed by the addition of 5 vol % of water (Figure S3b). The presence of protic solvent makes the photoreaction cleaner, suggesting that a photoinduced heterolysis of the axial group affords the TATA cation and the carbanion of axial group. The difference in the formation of side products between 1 and 2 can be attributed to the difference in the acidity between phenylacetylene and benzene; phenylacetylene has higher acidity, so that the phenylethynyl group is considered to dissociate cleanly.

For the phenylethynyl derivative **2**, the photoreaction affording the TATA cation was monitored by ¹HNMR in ethanol- d_6 . Upon UV irradiation, the signals corresponding to the TATA cation and phenylacetylene appeared as expected (Figure 4). No acetylenic proton was observed around 3.4 ppm after UV irradiation probably due to exchange with deuterium (red arrow, in Figure 4). Since no other peaks were observed after UV irradiation, the quantitative photocleavage reaction of **2** was also supported by ¹HNMR.

In a marked contrast to 1–4, the photoreactions of compounds 5 and 6 were significantly slow (Figures 3e–3g). According to

Table 1. Quantum yields of photocleavage reaction upon UV irradiation $^{\rm a}$

Compd	Quantum yield ^b	Orbital energyc/eV		HOMO-LUMO
	$(arPsi_{ m r})$	HOMO	LUMO	gap/eV
1	0.013	-5.25	-0.75	4.50
2	0.56	-5.29	-1.22	4.07
3	0.45	-5.22	-0.88	4.34
4	0.35	-5.28	-2.26	3.02
5	< 0.01	-5.33	-2.84	2.49
6	< 0.01	-5.30	-2.76	2.54

^aBy irradiation with 313 nm light. ^bMeasured in ethanol. ^cCalculated at B3LYP/6-311g(2d,p)-SCRF(PCM)//6-31g(d) level.

control experiments under dark condition, the process of thermal cleavage reaction from the TATA leuco derivative to the TATA cation was found to compete with the photoreaction for **5** and **6** (Figures S6–S8). Analysis by the Eyring plot gave the activation free energy of the thermal reaction for **5** as $\Delta G^{\ddagger} = 101 \text{ kJ mol}^{-1}$ at $25 \text{ °C} (\Delta H^{\ddagger} = 95 \text{ kJ mol}^{-1}, \Delta S^{\ddagger} = -20 \text{ J K}^{-1} \text{ mol}^{-1})$ (Figure S9). On the basis of these parameters, the halflife ($t_{1/2}$) of **5** in ethanol is 14 h at 25 °C, which is significantly shorter than that of **2** ($t_{1/2} = 10$ days, Figure S10). In the case of compounds **1–4**, the photochemical process was dominant, so that the thermal process was not easily discerned. For compound **6**, a small change in the absorption spectrum was also detected around 350 nm, which is due to the *cis–trans* photoisomerization of the azobenzene moiety. The photoisomerization of **6** became more distinct in toluene²⁰ (Figure S11).

The quantum yield of the photocleavage reaction was investigated in ethanol by monitoring the increase of absorbance at 525 nm upon UV irradiation (Table 1). Compared to the quantum yield of the phenyl derivative 1 ($\Phi_r = 0.013$), those of the arylethynyl derivatives 2–4 were significantly large ($\Phi_r = 0.35$ – 0.56). On the other hand, the quantum yields of the 10-cyano-9anthrylethynyl derivative 5 and the 4-(phenyldiazenyl)phenylethynyl derivative 6 were notably small ($\Phi_r < 0.01$). The difference in Φ_r between 1 and 2 can be explained by the presence or absence of the ethenyl group. The difference in Φ_r among 2–6 should be caused by the substituent effect and difference in the aromatic framework, i.e., benzene or anthracene.

In order to investigate the difference in the photoreactivity, time-dependent density functional theory (TD-DFT) calculations were performed on 1-6 at the B3LYP/6-311g(2d,p)//6-31g(d) level. The solvent effect was taken into account by using the selfconsistent reaction field (SCRF) with the polarizable continuum model (PCM). HOMOs of the leuco derivatives mainly localize at the TATA moiety while LUMOs localize at the axial groups (Figure S12). According to the contributions of molecular orbitals (MOs) calculated by TD-DFT, the lowest energy excited state has an intramolecular charge-transfer (CT) property from the TATA moiety to the axial groups. The LUMO energies were significantly lowered as the acceptor ability of axial groups increased; the LUMO energies of the 10-cyano-9-anthrylethynyl derivative 5 $(-2.84 \,\mathrm{eV})$ and 4-(phenyldiazenyl)phenylethynyl derivative 6 (-2.76 eV) are lower than that of the 9-anthrylethynyl derivative 4 (-2.26 eV) and the phenylethynyl derivative 2 (-1.22 eV). In contrast, the HOMO energies of 1-6 were almost constant (ca. -5.3 eV), which is attributed to the localization of HOMOs at the TATA moiety. Therefore, the HOMO-LUMO gap efficiently

decreased by introducing an electron-withdrawing group into the axial group. It is noted that there is a rough correlation between the LUMO energy and the photoreactivity; the quantum yield of the photocleavage reaction is small when the acceptor ability of the axial group is high (Table 1).

In conclusion, TATA leuco derivatives bearing different axial groups at the central carbon atom were synthesized and their photoreactivity was investigated. Owing to the good donor property of the TATA framework, a typical CT character was observed upon photoexcitation. It was found that the photo-cleavage reaction becomes clean and effective in the following conditions: (i) in polar media, (ii) in the presence of a protic solvent, and (iii) with a high LUMO energy of the axial group. These observations are of importance for the design of smart photoresponsive materials that can release small molecular components upon photoirradiation, especially on a 2-dimensional surface, via a photochemical reaction.

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Supporting Information is available electronically on J-STAGE.

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