New Type of Photochromism in Thioxanthene-10,10-dioxide Derivatives Based on Their Photoresponsive Acidity Change

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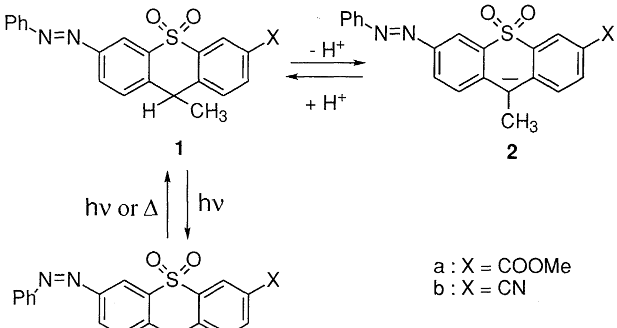
3-Methoxycarbonyl-9-methyl-6-*trans*-phenylazo- and 3-cyano-9-methyl-6-*trans*-phenylazothioxanthene-10,10-dioxide were synthesized. They reveal a property as a carbon acid based on the proton dissociation at C(9)-H, and the dissociation constants are much larger in their *trans*-azo form than the *cis* form. Their conjugate bases possess absorption band at around 670 nm. Developing and bleaching of the color are linked with the *trans* - *cis* photoisomerization of the phenylazo group.

Photoresponsive molecules have been a subject of much recent interests because of their potentiality for wide range of molecular devices, and a variety of photoresponsive molecules with various kind of property change have been developed.[1] However, only a few studies [2] have focused on the light-driven acidity change of molecules to our knowledge. In the present letter, we would like to report our preliminary model for the light-driven acidity change of molecules.

We intended to control the stability of the conjugate base of an acidic molecule by the structural change of a substituent caused by photoirradiation. Thioxanthene-10,10-dioxide was chosen as a fundamental molecular skeleton because the molecule would possess a property as a carbon acid due to the 14π aromatic delocalization of its conjugate base formed by C(9)-H proton dissociation through the vacant *d*-orbital of the sulfur atom. Photoresponsive *trans*-phenylazo group was introduced at one of the *para* positions to C(9) with an expectation that the photoinduced *trans-cis* isomerization of the substituent would have effect on the stability of the conjugate base. In addition to this, the molecule was derivatized by a methoxycarbonyl or cyano group at the other *para* position to C(9) in order to facilitate the proton dissociation at C(9)-H. Thus, 3-methoxycarbonyl- (**1a**) and 3-cyano-9-methyl-6-*trans*-phenylazothioxanthene-10,10-dioxide (**1b**) were synthesized,[3] and their photo-driven property changes were examined.



3 **Scheme 1.**

An electronic spectrum of **1a** in chloroform or in acetonitrile was very similar to that of azobenzene, and upon irradiation at 366 nm spectral changes were observed as follows. In an acetonitrile solution, for example, the principal ππ* absorption band at around 330 nm decreased and the nπ* absorption at around 440 nm increased slightly accompanied by distinct isosbestic points at 273 nm and 379 nm. This spectral change implied the *trans* to *cis* isomerization of the phenylazo group.[4] Prolonged irradiation afforded a photostationary mixture with a composition of **1a** : **3a** = 1 : 6.3. Upon irradiation to the nπ* band with a High-pressure mercury lamp fitted with a Toshiba L-39 filter (λ>390 nm, mainly 404 nm and 436 nm of the Hg-arc), the reverse reaction (**3a** to **1a**) took place to give a photostationary state of **1a** : **3a** = 7.4 : 1. The spectral feature as well as its change was also the same for the cyano derivative **1b**. On the other hand, in the electronic spectra of **1a** in dry N, N-dimethylformamide (DMF) a new absorption band appeared at λ_{max} = 667 nm as shown in the spectrum (a) of Figure 1. Upon addition of t-BuOK, the intensity of the band increased (the spectrum (b) in Figure. 1) without any change in its shape. The fact indicates that the new band at 667 nm is the absorption due to the conjugate base (**2a**) formed by the proton dissociation at C(9)-H of **1a** . Based on the comparison of the absorbance of the band in the presence of an enough amount of t-BuOK (spectrum (b)) with that in the absence of t-BuOK (spectrum (a)), it was estimated that about 33% of **1a** dissociated into its conjugate base **2a** in DMF under the conditions for measuring the spectrum (a). A similar band was observed at λ_{max} = 650 nm when **1a** was dissolved in acetonitrile containing triethylamine (Figure 2). In a similar manner, the degree of the proton dissociation was determined to be 0.14 for a solution of [**1a**] = 2.46×10^{-5} mol dm^{-3} in acetonitrile containing 0.072 mol dm^{-3} triethylamine.

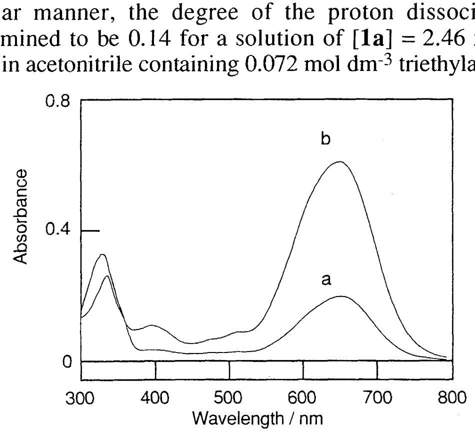


Figure 1. Electronic spectra of a solution of **1a** in DMF, [**1a**] = 1.23×10^{-4} mol dm^{-3}, (a) without t-BuOK, and (b) after adding an excess amount of t-BuOK. A cell with a light path length of 1 mm was used.

As mentioned above, **1a** and its conjugate base **2a** coexist at equilibrium in an acetonitrile solution containing triethylamine. As shown in the initial spectrum in Figure 2, both of the principal absorptions for **1a** and **2a** were observed at λ_{max} = 333 nm and at λ_{max} = 650 nm, respectively. No spectral change was observed when the band at 650 nm was irradiated with a 500 W halogen lamp fitted with a Toshiba Y51 filter (λ > 500 nm). On the other hand, upon irradiation at 366 nm, the absorption at 333 nm decreased with the concomitant decrement of the band at 650 nm. Both the absorption bands were recovered thermally and/or photochemically (404 nm and 436 nm lights which were effective for the *cis* to *trans* isomerization). The spectra at 650 nm obtained at several irradiation time intervals were normalized at their λ_{max}, and all the resulting spectra were superimposable with each other. This fact indicates that the chemical species responsible for the absorption band did not change during the irradiation time. These phenomena can be explained based on Scheme 1, that is, the *cis* isomer (**3a**) is much less acidic than **1a**, and no detectable amount of the conjugate base of **3a** exists under the conditions employed. Irradiation at 366 nm decreases the concentration of **1a** due to the *trans* to *cis* isomerization of **1a**, and the concentration of **2a** concomitantly decreases because **2a** exists in an equilibrium with **1a**. The quantitative conversion of **1a** to **3a** could not be attained because the photoisomerization reached to a photostationary state, and therefore, the band at 650 nm did not completely disappear even after prolonged irradiation at 366 nm.

It was attempted to confirm that the degree of proton dissociation is negligibly small for the *cis*-isomer by using a sample of **3a** containing as small amount of **1a** as possible. Though **3a** was separated carefully from a photostationary mixture in chloroform by HPLC, the sample obtained still contained small amount of **1a** due to the thermal isomerization of **3a** during the procedure. In the spectrum measured immediately after dissolving the sample, only the band at 650 nm due to contaminating **1a** was observed in the region of wavelengths longer than 500 nm. The spectrum measured immediately after dissolving **3a** in DMF containing t-BuOK was identical with the spectrum (a) in Figure 1. This fact indicates that the strong base abstracts the proton at the C(9) of **3a** and the thermal isomerization of the conjugate anion to **2a** is very fast.

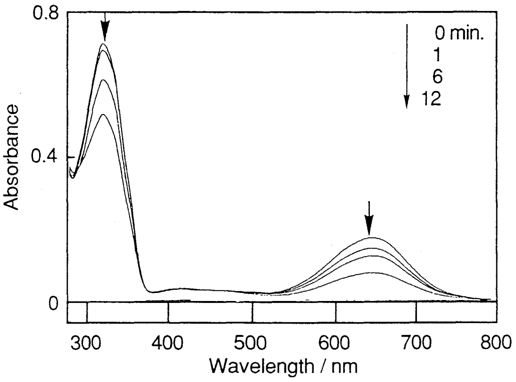


Figure 2. Electronic spectra following the photolysis (366 nm) of a solution of **1a**, [**1a**] = 2.46 x 10^{-5} mol dm^{-3}, in acetonitrile containing triethylamine, [NEt_3] = 0.072 mol dm^{-3}.

In the case of **1b**, the absorption due to its conjugate base (**2b**) could be observed at λ_{max} = 640 nm in acetonitrile even in the absence of the amine (Figure 3), and the degree of the proton dissociation was *ca.* 0.02 at a concentration of [**1b**] = 2.7 x 10^{-5} mol dm^{-3}. The spectral changes upon irradiation was similar to those of **1a**.

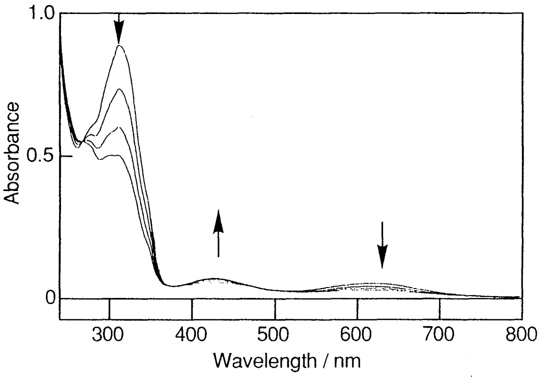


Figure 3. Electronic spectra following the photolysis (366 nm) of a solution of **1b**, [**1b**] = 2.7 x 10^{-5} mol dm^{-3}, in acetonitrile.

The σ_p^- value for *trans*-phenylazo group was reported to be 0.7 that is comparable to the value (0.73) for alkoxycarbonyl group (COOR).[5] This indicates the considerable ability of phenylazo group to stabilize an anion at the *para*-benzylic position. For example, the acidity of *p-trans*-phenylazophenol (pKa = 8.38) is much stronger than phenol (pKa = 10.0).[6] Thus, the proton dissociation of **1** should be facilitated by the phenylazo group at the C(6) position in cooperation with the methoxycarbonyl or cyano group at the C(3) position. Actually, in the case of 3-methoxycarbonyl-9-methylthioxanthene-10,10-dioxide, in which *trans*-phenylazo group is absent, no absorption for its conjugate base was observed in the slightly basic media employed in this study. The anion stabilizing ability of *trans*-phenylazo group is considered mainly due to the π delocalization of the charge. The group would lose the ability when it isomerizes to *cis*-form because of the loss of the co-planarity of the Ar-N=N-Ar' π-moiety. In connection with this, it is informative to refer to an electron-repelling interaction observed between the azomethine lone-pair and the aminophenyl group in *p*-amino-N-benzalaniline.[7] If it is also the case for the *cis*-phenylazo group, the substituent might act even as an electron-donating group.

Although azobenzene compounds appear to deepen in color upon *trans* to *cis* isomerization due to an increase in the strength of the $n\pi^*$ absorption, one drawback to photochromism of these molecules is the lack of a significant color change.[8] The molecules presented here are interesting from the viewpoint of an amplification of color change, because they are colored only in their *trans*-form. However, there remain problems, that is, thermally unstable nature of the *cis*-forms, and further studies are in progress.

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References and Notes

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3 **1a**: mp 220-221 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.80 (1H, d, J = 1.5 Hz), 8.68 (1H, d, J = 1.8 Hz), 8.25 (1H, dd, J = 8.1Hz, J = 1.8 Hz), 8.13 (1H, dd, J = 8.1 Hz, J = 2.1 Hz), 7.98-7.95 (2H, br.), 7.63 (1H, d, J = 8.4 Hz), 7.59 (1H, d, J = 8.1 Hz), 7.58-7.52 (3H, br.), 4.47 (1H, q, J = 7.5 Hz), 3.98 (3H, s), and 1.87 ppm (3H, d, J = 7.5 Hz); IR (KBr) 1730, 1298, 1133 and 1116 cm^{-1}; HRMS Found: 406.0981, Calcd for $C_{22}H_{18}N_2O_4S$: 406.0987. **1b**: mp 248-249 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.65 (1H, d, J = 2.1Hz), 8.43 (1H, d, J = 1.8 Hz), 8.15 (1H, dd, J = 8.4 Hz, J = 1.8 Hz), 7.97-7.94 (2H, m), 7.85 (1H, dd, J = 8.1 Hz, J = 1.8 Hz), 7.64 (2H, d, J = 8.1 Hz), 7.56-7.53 (3H, m), 4.48 (1H, q, J = 7.5 Hz), and 1.87 ppm (3H, d, J = 7 .5 Hz); IR (KBr) 2237, 1308 and 1138 cm^{-1}; HRMS Found: 373.0874, Calcd for $C_{21}H_{15}N_3O_2S$: 373.0884.

4 *cis*-Azobenzene reveals an intense band at λ_{max} = 250 nm with a shoulder tailing to around 350 nm (Ref. 8, p. 507). Similarly, **3a** and **3b** do not show any distinct absorptions at the wavelength region longer than 260 nm other than the weak $n\pi^*$ band.

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