Photochromism of Aza-aromatics with Hydroxy Group. Intermolecular Proton Transfer in Glassy Solution

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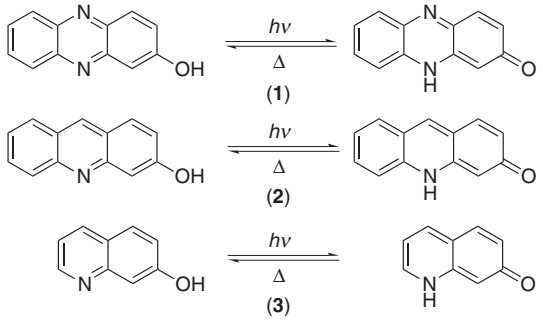
When solutions of 2-hydroxyphenazine (**1**), 3-hydroxyacridine (**2**), and 7-hydroxyquinoline (**3**) were irradiated with UV light at 77 K, they became deeply colored. The color of the solutions reverted to the original one, when they were left in the dark at 77 K or at a higher temperature. We ascribe the photochromism to proton tautomerization, which is most likely induced by an intermolecular proton transfer in the excited state.

Proton transfer is a fundamental process in chemistry and biology.[1] If proton transfer causes proton tautomerization, the π-electronic state of the molecule and accordingly the color of the substance may change.[2,3] Such a substance might exhibit photochromism[4] if proton tautomerization is induced photochemically.

We report here a new photochromism for a series of aza-aromatics with a hydroxy group, 2-hydroxyphenazine (**1**), 3-hydroxyacridine (**2**), and 7-hydroxyquinoline (**3**), in 2-methyltetrahydrofuran (MTHF) at 77 K.



When MTHF solution of **1** was irradiated with UV light at 77 K,[5] the color of the glassy solution changed from pale yellow to purple-red. The color gradually reverted to the original one when the solution was left in the dark at 77 K and immediately disappeared at a higher temperature at which the glass matrix melts. The photo-induced coloration was not observed at room temperature.

Figure 1 shows the electronic absorption spectra for the photochromism of **1**. The spectrum recorded before irradiation at 77 K exhibits absorption bands in a short-wavelength region through ca. 460 nm. When the solution was irradiated with UV light at $\lambda = 365$ nm,[6] new absorption bands emerged in the long-wavelength region (ca. 450–610 nm) and the short-wavelength absorption bands decreased in intensity.

The spectral change suggests that a proton tautomerization from the OH to NH forms takes place after the UV irradiation. The long-wavelength absorption bands are assigned to the NH form, because they are comparable in wavelength to those of the NH form in an aqueous ethanol solution.[7]

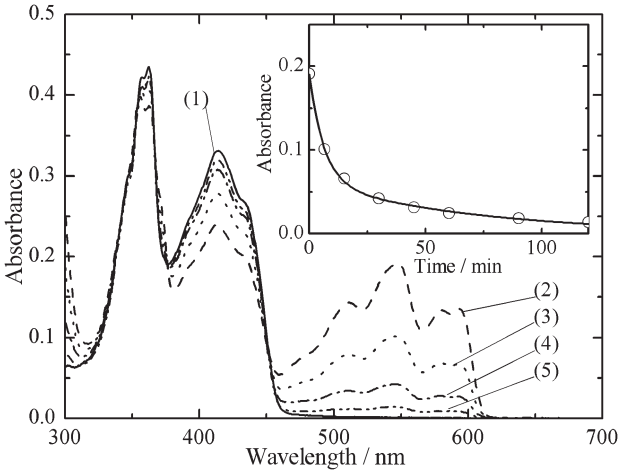


Figure 1. Electronic absorption spectra of **1** in MTHF at 77 K, 2.1×10^{-4} M, path length 2 mm. Curves (1) before irradiation, (2)–(5) after irradiation, 0, 6.5, 30, and 120 min, respectively. The inset represents the decay of the absorbance at 548 nm. The decay curve was fitted to an equation $y = 0.13\exp(-0.16t) + 0.062\exp(-0.014t)$, where y is the absorbance at the time t, with the correlation parameter of 1.00.

When the solution was left in the dark at 77 K, the long-wavelength absorption bands decreased in intensity and almost disappeared after two hours. The decay kinetics was fitted to a double exponential function, as shown in the inset of Figure 1.

Compounds **2** and **3** also exhibited a similar photochromism in MTHF at 77 K (Figures 2 and 3).

Upon irradiation with UV light ($\lambda = 365$ nm), the colorless solution of **2** turned red. The solution gradually reverted to its colorless state, when it was left in the dark at 77 K. The photo-induced colored species is assigned to the NH form as in **1**.[8] The decay kinetics followed a double exponential equation, as shown in the inset of Figure 2.

A colorless solution of **3** turned yellow upon UV irradiation ($\lambda = 313$ nm). The photo-induced colored species, which is assigned to the NH form,[9] persisted at 77 K, in contrast to **1** and **2**; the spectra hardly changed for two hours at 77 K, indicating that the photochemically produced NH form is much more stable in **3** than in **1** and **2**, in the glass matrix.

The photochromism can be explained if we assume that a proton transfer proceeds in the excited state and causes proton tautomerization from the OH to the NH forms.[10] The proton transfer has the following features.

Firstly, proton transfer cannot proceed intramolecularly in **1**, **2**, and **3**, because the proton-accepting N atom is too distant

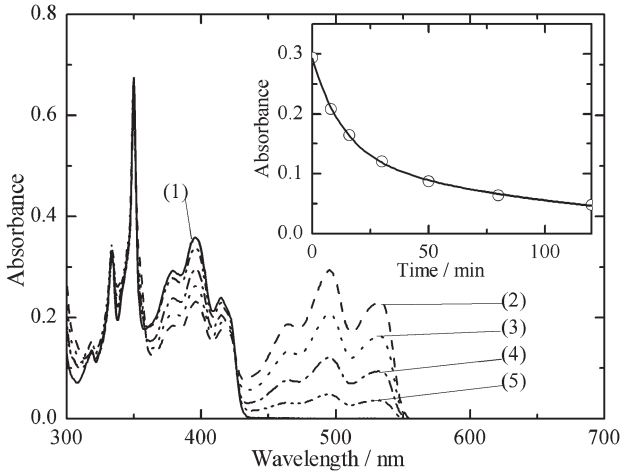


Figure 2. Electronic absorption spectra of **2** in MTHF at 77 K, 2.6×10^{-4} M, path length 2 mm. Curves (1) before irradiation; (2)–(5) after irradiation, 0, 8, 30, and 120 min, respectively. The inset represents the decay of the absorbance at 495 nm. The decay curve was fitted to an equation $y = 0.16\exp(-0.075t) + 0.13\exp(-0.0087t)$, where y is the absorbance at the time t, with the correlation parameter of 1.00.

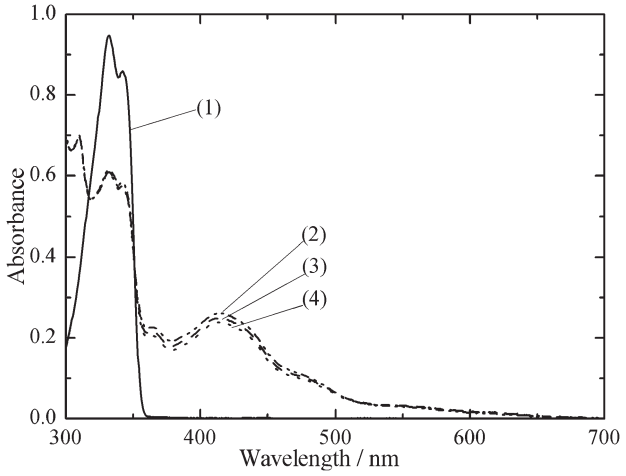


Figure 3. Electronic absorption spectra of **3** in MTHF at 77 K, 5.9×10^{-4} M, path length 2 mm. Curves (1) before irradiation; (2)–(4) after irradiation, 0, 60, and 120 min, respectively.

from the proton-donating OH group in the molecule.[11,12] The fact that the geometric conditions are unfavorable for an intramolecular process suggests that the proton transfer proceeds intermolecularly.[11,13–15] In such an intermolecular proton transfer, solvent molecules may not be involved, because the proton transfer proceeded in the aprotic solvent MTHF. The occurrence of the intermolecular proton transfer in a rigid glass matrix suggests that an aggregate is formed through intermolecular hydrogen bonding at a low temperature, and that the proton transfer proceeds in the aggregate.[3,15]

Secondly, the thermal color decay is very slow.[16] The decay would be much faster if the aggregate kept its structure in the solution. The slow decay can, therefore, be considered as an indication that the structure of the aggregate changes after the production of the NH form.

Thirdly, the decay kinetics could not be fitted to a single exponential but to a double exponential equation, indicating that the photoinduced colored species consist of two NH forms with different lifetimes; for **1**, 68% have a short lifetime of 6.4 min and 32% have a much longer lifetime of 71 min; for **2**, 55% have a lifetime of 13 min and 45% have a lifetime of 115 min.

In summary, the present paper reports the discovery of a new photochromism induced by intermolecular proton transfer for a series of aza-aromatics with a hydroxy group, **1**, **2**, and **3** in MTHF solution at 77 K. Further investigation on the photochromism is now in progress.

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