ESIPT-Induced photocyclization of *N*,*N*′-diphenyl-1,5-dihydroxy-9,10-anthraquinone diimine

Keiji Kobayashi,*[a]† Mayumi Iguchi,[a] Tatsuro Imakubo,[a] Koichi Iwata[b] and Hiro-o Hamaguchi[b]

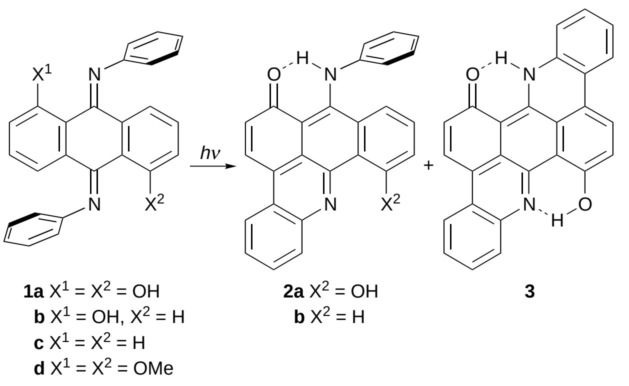
[a] *Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153 Japan*

[b] *Department of Chemistry, Graduate School of Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113 Japan*

Photolysis of *N*,*N*′-diphenyl-1,5-dihydroxy-9,10-anthraquinone diimine affords acridine-condensed aromatic compounds *via* excited-state intramolecular proton-transfer, as revealed by time-resolved IR spectroscopy.

Excited-state intramolecular proton-transfer (ESIPT) has been extensively investigated in relation with photochromic materials and UV stabilizers.[1] In ESIPT phenomena, mostly observed in salicylates[2] and salicylideneanilines,[3] the photoexcited keto form is produced by rapid proton transfer from the photoexcited enol form and undergoes deactivation nonradiatively and/or radiatively to the ground-state keto form, which regenerates thermally the original enol. In such a reversible phototautomeric cycle, the ESIPT-induced excited enol is fated to follow the tautomeric pathway and other relaxation processes have rarely been encountered. We report herein a novel photochemical reaction which is, to the best of our knowledge, the first irreversible transformation *via* ESIPT in a phototautomeric system.

N,*N*′-diphenyl-1,5-dihydroxy-9,10-anthraquinone diimine **1a** in benzene was irradiated at room temperature, using a 100 W high pressure Hg lamp through a Pyrex filter, under argon for 48 h (Scheme 1). The photoproducts were chromatographed on silica gel and acridine-condensed compounds **2a** and **3** were obtained in 64 and 14% yields, respectively. Irradiation of **2a** under the same conditions as used for **1a** gave rise to **3**, indicating that **3** is a secondary photoproduct of **1a**. The photocyclization was also accomplished in monohydroxy derivative **1b**; irradiation of **1b** in benzene for 54 h led to the formation of **2b** (18%). The structure of **2a** was deduced from an X-ray crystallographic analysis‡ and that of **2b** was proved on the basis of its spectral properties. The formation of **2a** and **2b** is ascribed to aromatic cyclization at C(4) accompanied by enol-to-keto tautomerization of the hydroxy group at C(1). These common characteristics of the photoproducts indicate that the same type of the photoreaction occurred in **1a** and **1b**.



Scheme 1

The irradiation of **1c** and **1d**, which have no hydroxy groups at the peri positions, caused no photoreactions even after irradiation for 60 h. The absence of photoreactivity in **1c** and **1d** clearly shows that the hydroxy group at the peri position plays an essential role in promoting the photocyclization. Furthermore, the role of the hydroxy group cannot be ascribed to its electron-donating nature, since the methoxy derivative was not photoreactive. The above results provide chemical evidence for the involvement of ESIPT in the photocyclization. It should also be noted here that compound **1a** exists almost completely in the enol form (96%) under the fast equilibrium with the keto form in the ground state, as monitored by temperature dependent ^{1}H and ^{13}C NMR spectroscopy.

The intervention of the ESIPT in the photocyclization was probed by means of sub-microsecond time-resolved IR spectroscopy,[4] which can detect the increase in the ground-state keto form upon irradiation. Fig. 1 shows the transient IR spectra of **1a** in CCl$_4$ following excitation at 262 nm with 5 ns pulses.§ Several new positive absorption bands appear following excitation, in addition to negative peaks due to the ground-state depletion. Those are ascribed to two transient species; one (**A**: ~1550 cm^{-1}) decays rapidly and almost disappears after 200–300 µs, while the other (**B**: 1630 and 1240 cm^{-1}) decays very slowly and still remains after 800 µs. The lifetimes of transient species **A** and **B** were estimated to be 80–90 µs and 1.3 ms, respectively, by the curve fitting of Fig. 2, assuming a simple exponential decay.

Transient species **B** could be assigned to the keto imine tautomer in the ground-state, since its absorptions 1630 and 1240 cm^{-1} are attributed to vibration of the hydrogen bonded C=O group and the C–N stretching, respectively. With respect to transient species **A**, we postulate an intramolecular cycloadduct as the most plausible candidate based on its IR absorption at *ca*. 1550 cm^{-1}, corresponding to the absorption

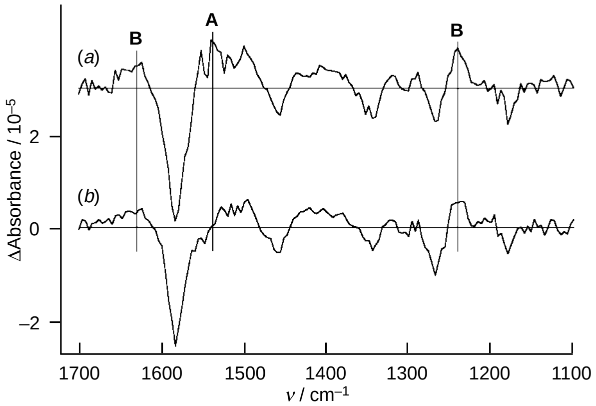


Fig. 1 Time-resolved IR spectra of **1a** after (*a*) 0–20 and (*b*) 200–800 µs of excitation. The figure is represented as a difference spectrum. Negative peaks represent a decrease in the infrared absorption due to the depletion of the ground state and positive peaks correspond to an increase in the absorption by the photogenerated transient species.

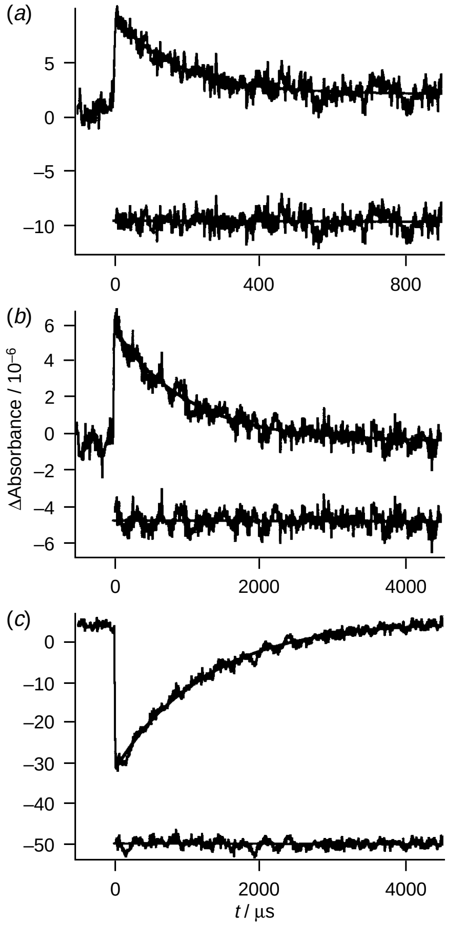
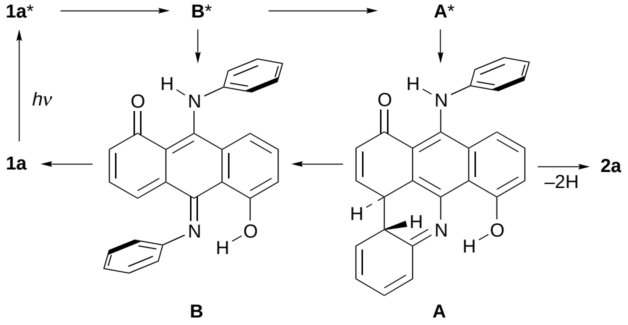


Fig. 2 Decay curves of the absorption bands at (*a*) 1550 (**A**) and (*b*) 1630 cm^{-1} (**B**), and (*c*) recovery curve of the absorption band at 1584 cm^{-1} (**1a**)

band of a C=N bond incorporated in the cyclic framework. Thus we can depict the fate of the ESIPT as shown in Scheme 2.

No photoproduct **2a** could be detected after the time-resolved measurements. The bubbling of argon through the reaction is considered to work effectively to prevent oxidation of transient species **A** to give **2a**. Thus, all the spectral changes were reversible. However, when argon was not bubbled through the reaction, the formation of **2a** was confirmed by its UV absorption at 530 and 460 nm; the formation of **2a** upon photolysis of **1a** on a preparative scale is ascribed to inefficient argon bubbling. Irradiation of a cautiously degassed sample of **1a** in an NMR sample tube suppressed the formation of **2a** down to a few percent.

The formation of polycyclic systems by intramolecular photocyclization is a common process for several types of aromatic compound. However, benzilideneanilines and azobenzenes fail to undergo aromatic photocyclization under the usual conditions; it has been reported that addition of sulfuric acid or Lewis acids promotes the heteroaromatic cyclization.[5] Thus this work demonstrates a novel photocyclization promoted by ESIPT and hence provides an example of deactivation other than phototautomerization that is possible for the ESIPT of a tautomeric system.



Scheme 2

Notes and References

† E-mail: ckobak@komaba.ecc.u-tokyo.ac.jp

‡ *Crystal data* for **2a**: Rigaku AFC-5S diffractometer, Mo-Kα radiation, λ = 0.71073 Å, graphite monochrometer, T = 295 K. Data collection, solution and refinement: ω–2θ, direct methods using the SIR 88 program, followed by Fourier synthesis, TEXSAN computer program. $C_{26}H_{16}N_2O_2$, M_w = 388.43, triclinic, space group $P\bar{1}$, a = 11.0202(14), b = 11.3768(14), c = 8.7455(10) Å, α = 110.652(9), β = 94.004(11), γ = 113.733(9)°, U = 910.0(2) Å^3, Z = 2, D_c = 1.417 g cm^{-3}, crystal size 0.40 × 0.15 × 0.10 mm. 4399 reflections measured in the range $4 < 2\theta < 55°$, 1436 unique reflections with $|F_o| > 3\sigma|F_o|$. 335 parameters. R = 0.045 and R_w = 0.026. CCDC 182/764.

§ We also carried out time-resolved experiments at 349 nm, despite some experimental difficulties associated with low absorbance at this wavelength, and confirmed the formation of **2a** when argon was not bubbled. Thus we observe the same photoexcited process in the time-resolved experiments and in the preparative-scale experiments.

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Received in Cambridge, UK, 16th December 1997; 7/09022F