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# Intramolecular proton transfer in the triplet state of 1-(acylamino)anthraquinones

Shin-ichi Nagaoka *, Syutaro Yamamoto, Kazuo Mukai

*Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, 790-77, Japan*

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**Abstract**

Intramolecular proton transfer in the triplet state of 1-(acylamino)anthraquinones has been studied by means of transient absorption spectroscopy. The substituent and solvent effects were observed and were discussed in conjunction with the energy-state diagram. The singlet–triplet energy-gap of the proton-transferred form is much less than that in the normal form. © Elsevier Science S.A.

*Keywords:* Excited state intramolecular proton transfer; 1-(Acylamino)anthraquinone; Transient absorption spectroscopy

## 1. Introduction

The excited-state intramolecular proton transfer (ESIPT) of hydrogen-bonded molecules has elicited considerable experimental and theoretical interest [1–7]. It is a very simple chemical process and is of great interest in view of its use as a polymer-protecting agent and the possibilities of making a proton-transfer laser and an information storage device at the molecular level.

In previous papers [8,9], Smith and coworkers studied ESIPT in the singlet state (ESIPT-S) of 1-(acylamino)-anthraquinones (AYAAQs) and observed anomalous substituent and solvent effects on the ESIPT-S. AYAAQs were established as a new class of ESIPT molecules, in which nitrogen acts as the proton donor. The use of acylamino groups as proton donors allows for fine tuning of the driving force and adds a new dimension for studying ESIPT reactions. Subsequently, Nagaoka and Nagashima showed that the substituent and solvent effects on ESIPT-S of AYAAQs can be explained by considering the nodal pattern of the wave function (Fig. 1) [10].

However, in the previous studies of AYAAQs [8–10], attention was mainly focused on the low-lying excited singlet states. Much less is known about the excited triplet state. In the present paper, we have thus studied ESIPT in the low-lying triplet states (ESIPT-T) of AYAAQs by means of transient absorption spectroscopy. Interpretation of the experimental results is made by using the idea based on the nodal pattern of the wave function.

The molecular structures of AYAAQs are given in Fig. 1. We confine our attention to $\pi$-electrons. A simple eight-state diagram has proven to be a useful starting point for describing many facets of ESIPT-T behavior (Fig. 1). In Fig. 1, $S_0$, $S_1$, $T_1$ and $T_n$ denote the ground-state, the lowest-excited-singlet-state, the lowest-excited-triplet-state and the upper-excited-triplet-state, respectively, and (N) and (T) stands for the normal 9,10-*keto* form and the 1,10-*keto*-type tautomeric form, respectively.

## 2. Experimental

1-(trifluoroacetylamino)anthraquinone (TFAQ), 1-(chloroacetylamino)anthraquinone (CAAQ) and 1-(acetylamino)anthraquinone (AAAQ) were prepared according to a procedure similar to that reported previously [9]. Commercially obtained 1,8-dihydroxyanthraquinone (1,8-DHAQ) was purified by column chromatography on silica gel with chloroform and recrystallization from ethanol. 1,8-dimethoxyanthraquinone (1,8-DMAQ) was synthesized from 1,8-DHAQ according to a procedure similar to that reported previously [11]. It was necessary to use 10–20 times the molar quantity of dimethyl sulfate compared with 1,8-DHAQ.

* Corresponding author. Tel.: +81 89 9279592; fax: +81 89 9279590.


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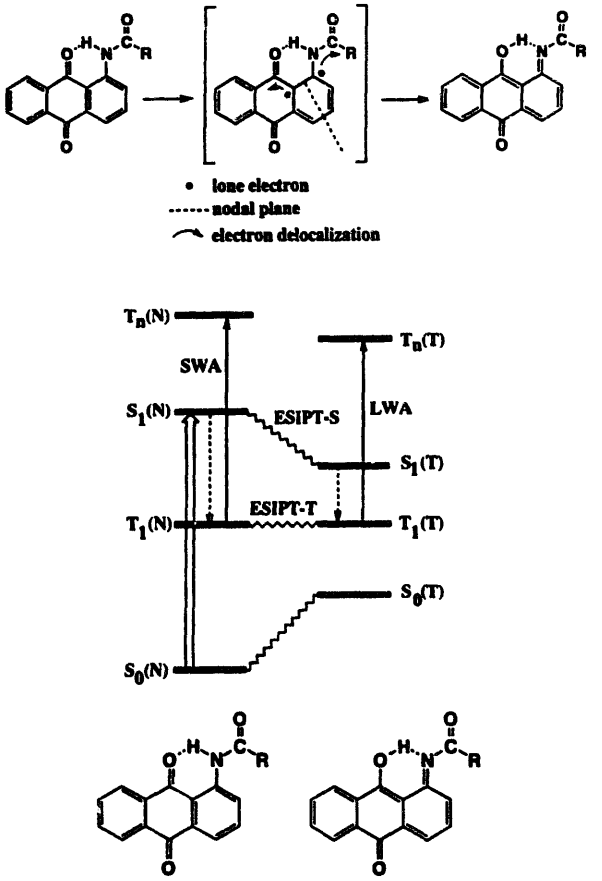


Fig. 1. Nodal plane model [10] for ESIPT, molecular structures of AYAAQs and simple eight-state diagram of ESIPT behavior in AYAAQs. An arrow with a double line and a dashed arrow denote photoexcitation and intersystem crossing (ISC), respectively. $R = CF_3$, TFAQ; $R = CH_2Cl$, CAAQ; $R = CH_3$, AAAQ.

Acetonitrile and hexane specially prepared for luminescence were obtained from Nacalai Tesque and were used without further purification. Dichloromethane was refluxed over $P_2O_5$ for 12 h and was then distilled. Benzophenone was purified by repeated sublimation.

Transient absorption spectra were obtained at room temperature with a Unisoku USP-500 pulse-flush spectrometer and the lifetime of the exciting light pulse was about 2 μs. The spectral range of flash-lamp excitation was 300–800 nm. The concentrations of samples were $10^{-4}$ to $10^{-3}$ M. A rectangular quartz cell (2 cm in light-path length) was used in the measurements of the transient absorption spectra. The sample solutions were usually bubbled through with nitrogen gas to remove dissolved oxygen. The transient absorption spectra were obtained at 2 μs after photoexcitation. In the measurements of the decay of the transient absorption, the sample solutions were degassed by means of the repeated freeze–pump–thaw method. The transient-absorption decay-profiles were well described by a monoexponential fit. The lifetime was independent of the sample concentration throughout the concentration range studied. The experimental error of the lifetime was less than ±7%.

## 3. Results and discussion

Fig. 2 and Fig. 3 show the transient absorption spectra of TFAQ and CAAQ in various solvents, respectively. The transient absorption spectrum of AAAQ in hexane (data not shown) is similar to that of CAAQ. Since these transient absorption spectra are quenched by oxygen, they are likely due to triplet–triplet absorption (T–T absorption). The T–T absorption spectra of CAAQ (Fig. 3) are similar to those of AAAQ in toluene and 1-(heptanoylamino)anthraquinone (HPAQ) in acetonitrile reported previously [9,12]. AYAAQs are suitable for detailed investigations of ESIPT-T, because they show strong T–T absorption without sensitizers at room temperature.

Two peaks can clearly be seen around 450 and 480 nm in the spectra of TFAQ in hexane (Fig. 2a). From the following

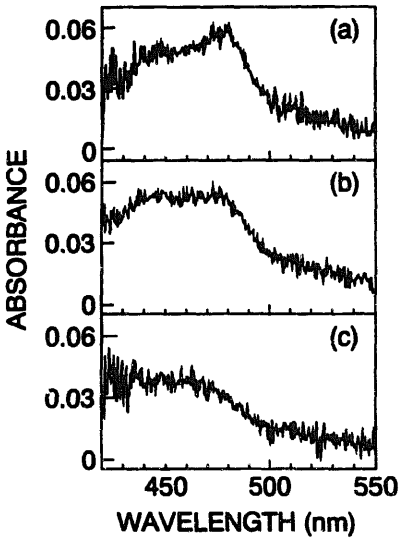


Fig. 2. Transient absorption spectra of TFAQ obtained in (a) hexane, (b) dichloromethane and (c) acetonitrile at room temperature.

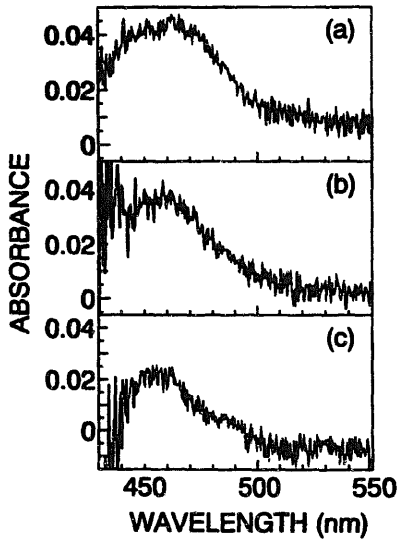


Fig. 3. Transient absorption spectra of CAAQ obtained in (a) hexane, (b) dichloromethane and (c) acetonitrile at room temperature.

reasons, the short and long wavelength absorption bands (SWA and LWA, respectively) are considered to be due to the 9,10-*keto*- and 1,10-*keto*-type forms, respectively ($T_1(N) \rightarrow T_n(N)$ and $T_1(T) \rightarrow T_n(T)$ transitions in Fig. 1, respectively).

First, the assignment is inferred from analogy with the solvent effect on ESIPT-S of AYAAQs, in which susceptibility to ESIPT-S in CAAQ and 1-(dichloroacetylamino)-anthraquinone decreases as the solvent polarity increases [8,9]. In Fig. 2, LWA intensity decreases as the solvent polarity increases. Accordingly, LWA is likely due to the proton-transferred 1,10-*keto*-type form.

Secondly, the substituent effect on ESIPT-S of AYAAQs also supports our view. As the electron withdrawing property of the substituent *R* in Fig. 1 increases, susceptibility to ESIPT-S increases; TFAQ is more susceptible to ESIPT-S than CAAQ [8,9]. In Fig. 2 and Fig. 3, TFAQ shows LWA in hexane, while CAAQ does not show it. Accordingly, LWA seems to correspond to the $T_1(T) \rightarrow T_n(T)$ transition.

The above-mentioned arguments could be strengthened if the T–T absorption spectrum from the $T_1(N)$ state of 1-(*N*-trifluoroacetyl-methylamino)anthraquinone (TFMAQ, *N*-methyl-derivative of TFAQ) were obtained. Accordingly, we prepared TFMAQ according to a procedure similar to that reported previously [9]. However, the transient absorption intensity of TFMAQ was negligible. Thus, we compared the transient absorption spectra of 1,8-DHAQ and 1,8-DMAQ (Fig. 4) instead of TFAQ and TFMAQ.

Since the transient absorption of 1,8-DHAQ and 1,8-DMAQ is quenched by oxygen, it is likely due to the T–T absorption. 1,8-DHAQ shows the T–T absorption around 475 nm, although 1,8-DMAQ shows it below 430 nm (Fig. 4). Methylation of 1,8-DHAQ results in a large blue-shift of the T–T absorption spectrum. Many 1-substituted anthraquinones have the $T_1$ states of ($\pi,\pi^*$) character with short lifetimes [13]. In fact, the lifetime of the T–T absorption of 1,8-DMAQ (430 nm) is very short (151 μs in EPA at 77 K). Although 1,8-DMAQ does not have intramolecular hydrogen bonds in contrast to 1,8-DHAQ, the $T_1$ state of 1,8-DMAQ seems to have a character of ($\pi,\pi^*$) as in the case of 1,8-DHAQ.

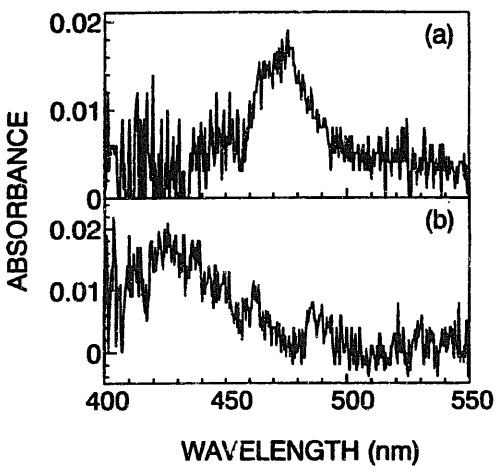


Fig. 4. Transient absorption spectra of (a) 1,8-DHAQ and (b) 1,8-DMAQ obtained in hexane at room temperature.

1,8-DHAQ favors ESIPT [14], while ESIPT is inhibited in 1,8-DMAQ. Thus, the T–T absorption of 1,8-DMAQ (430 nm) corresponds to the transition from the $T_1(N)$ state of 1,8-DHAQ. Accordingly, the T–T absorption of 1,8-DHAQ (475 nm) is considered to originate from the proton-transferred form. The T–T absorption from the $T_1(N)$ state of 1,8-DHAQ may be very weak or the decay of its triplet species may occur within the lifetime of the exciting light pulse ($\approx 2$ μs). The proton-transferred form (1,10-*keto* form) and the normal form (9,10-*keto* form) of 1,8-DHAQ's are likely to show the T–T absorption in the long and short wavelength ranges, respectively, as in the case of 2-(2′-hydroxyphenyl)benzothiazole [15]. These results support our view that SWA and LWA are due to the 9,10-*keto* form and the 1,10-*keto*-type tautomeric form of AYAAQs, respectively.

In Fig. 2, as the solvent polarity increases, the LWA intensity decreases in TFAQ. In contrast, LWA is negligible in CAAQ for all the solvents studied. From these results, it is concluded that the population of the $T_1(T)$ state in TFAQ decreases with increasing the solvent polarity, and that it is negligible in CAAQ for all the solvents studied.

Next, it should be examined whether or not ESIPT and intramolecular proton-back-transfer (ESIPBT) take place in the triplet manifold. Photosensitization is a useful method for such an examination. The stable species in the $S_0$ and excited singlet states of TFAQ in hexane are the normal 9,10-*keto* form and the 1,10-*keto*-type tautomeric form, respectively [8,9]. Thus, the $T_1(N)$ state of TFAQ is populated at the beginning in the photosensitization, while the $T_1(T)$ state is populated after $S_0 \rightarrow S_1(N)$ photoexcitation, $S_1(N) \rightarrow S_1(T)$ ESIPT-S and the subsequent $S_1(T) \rightarrow T_1(T)$ intersystem crossing (ISC). However, the T–T absorption spectrum of TFAQ which is photosensitized with benzophenone in hexane (data not shown) is very close to that obtained after the photoexcitation, the ESIPT-S and the subsequent ISC (Fig. 2a). Accordingly, it is suggested that equilibrium between the $T_1(N)$ and $T_1(T)$ states of TFAQ in hexane is nearly established within the lifetime of the exciting light pulse. The fact that the lifetimes of SWA and LWA of TFAQ in hexane (35 and 39 μs, respectively) are close to each other also supports our view.

Since TFAQ in acetonitrile favors ESIPT-S [8,9] and shows SWA predominantly (Fig. 2c), the stable species in the excited singlet and triplet states will be the 1,10-*keto*-type tautomeric form and the normal 9,10-*keto* form, respectively. After the $S_1(T) \rightarrow T_1(T)$ ISC, ESIPBT to the $T_1(N)$ state is likely to take place in polar solvents. From these results, it is concluded that ESIPT and ESIPBT occur in the triplet manifold along with ESIPT-S.

Next, we discuss the energy-state diagram of ESIPT behavior in AYAAQs. The above-mentioned solvent effect in TFAQ (Fig. 2) can be ascribed to the difference in dipole moment between the $T_1(N)$ and $T_1(T)$ states, as in the case

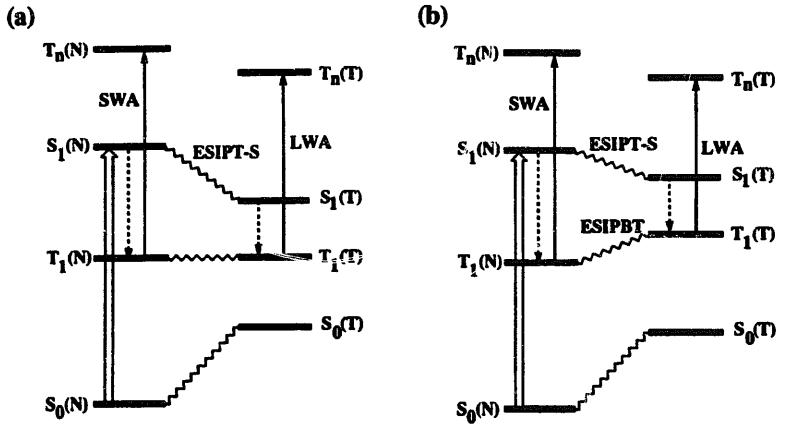


Fig. 5. Schematic energy-state diagram of ESIPT behavior in (a) TFAQ and (b) CAAQ in non-polar solvents. An arrow with a double line and a dashed arrow denote photoexcitation and ISC, respectively.

of the excited singlet state [10]. In TFAQ, the energy levels of the $T_1(N)$ and $T_1(T)$ states will be very close to each other (Fig. 5a) and the solvent polarity has a major influence on ESIPT-T.

In contrast, in CAAQ, the solvent polarity does not have a major influence on ESIPT-T, and CAAQ mainly shows SWA. In this molecule, the energy level of the $T_1(N)$ state will be much lower than that of the $T_1(T)$ state (Fig. 5b) and subtle effects from solvents will not have a large influence on the T–T absorption.

As shown in Fig. 5, the energy gap between the excited singlet and triplet states (S–T gap) in the normal 9,10-*keto* form is much larger than that in the 1,10-*keto*-type tautomeric form. Similar results were also obtained in ESIPT of other molecules; the triplet states corresponding to the $T_1(N)$ and $T_1(T)$ states are equilibrium in 2-(2-hydroxyphenyl)-benzoxazole and the $T_1(N)$ state is more stable than the $T_1(T)$ state in 2-(2-hydroxy-4-methylphenyl)benzoxazole, although the $S_1(T)$ states are more stable than the $S_1(N)$ states [16–19].

Probable explanation for the difference in S–T gap between the normal 9,10-*keto* form and the 1,10-*keto*-type tautomeric form is suggested in the following. We assume that the stable structures and the electron occupancy of the $S_1(N)$ and $S_1(T)$ states are close to those of the $T_1(N)$ and $T_1(T)$ states, respectively. If this is the case, the electrons keep out of one another's way better in the triplet than in the singlet state, or as it may be said that the electronic motions are better correlated in the triplet state, or there is better correlation in the triplet wave function. Owing to this correlation effect, the triplet state is lower in energy than the singlet state [20]. On the other hand, the reason for ESIPT of AYAAQs can be understood by considering the $\pi$-electron nodal pattern of the wave function [10]; lone electrons due to the nodal pattern in the lowest excited state and their delocalization result in ESIPT (Fig. 1). Owing to the electron delocalization, the above-mentioned correlation effect is expected to become small [20]; the energy levels of the singlet and triplet states approach each other as the delocalization becomes large. As a result, the S–T gap in the 1,10-*keto*-type tautomeric form is much less than that in the normal 9,10-*keto* form (Fig. 1).

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## References

[1] W. Klöpffer, Adv. Photochem. 10 (1977) 311.
[2] P.M. Rentzepis, P.F. Barbara, Adv. Chem. Phys. 47 (2) (1981) 627.
[3] D. Huppert, M. Gutman, K.J. Kaufmann, Adv. Chem. Phys. 47 (2) (1981) 643.
[4] P.F. Barbara, P.K. Walsh, L.E. Brus, J. Phys. Chem. 93 (1989) 29 (Feature Article).
[5] P.F Barbara, H.P. Trommsdorff (eds.), Chem. Phys. 136 (1989) 153–360.
[6] P.F. Barbara, M. Nicol, M.A. El-Sayed (eds.), M. Kasha Festschrift, J. Phys. Chem. 95 (1991) 10 215–10 524.
[7] H. Shizuka (ed.), Proc. of the 54th Okazaki Conf.: Dynamic Studies on Hydrogen Atom Transfer Reactions, Institute for Molecular Science, Gunma University, Okazaki/Kiryu, 1996.
[8] T.P. Smith, K.A. Zaklika, K. Thakur, P.F. Barbara, J. Am. Chem. Soc. 113 (1991) 4035.
[9] T.P. Smith, K.A. Zaklika, K. Thakur, G.C. Walker, K. Tominaga, P.F. Barbara, J. Phys. Chem. 95 (1991) 10 465.
[10] S. Nagaoka, U. Nagashima, Chem. Phys. 206 (1996) 353.
[11] E.C. Horning (ed.), Organic Syntheses Collective Vol. 3 (Wiley, New York, 1995) pp. 564–566.
[12] V.J.P. Srivatsavoy, B. Venkataraman, Chem. Phys. Lett. 174 (1990) 406.

[13] K. Hamanoue, Y. Kajiwara, T. Miyake, T. Nakayama, S. Hirase, H. Teranishi, Chem. Phys. Lett. 94 (1983) 276; K. Hamanoue, T. Nakayama, M. Shiozaki, Y. Funasaki, K. Nakajima, H. Teranishi, J. Chem. Phys. 85 (1986) 5698; K. Hamanoue, T. Nakayama, Y. Kajiwara, T. Yamaguchi, H. Teranishi, J. Chem. Phys. 86 (1987) 6654; T. Nakayama, T. Yamaguchi, K. Ushida, K. Hamanoue, S. Miki, K. Matsuo, Z. Yoshida, Chem. Phys. Lett. 148 (1988) 259.
[14] G. Smulevich, J. Chem. Phys. 82 (1985) 14.
[15] S. Nagaoka, A. Itoh, K. Mukai, U. Nagashima, J. Phys. Chem. 97 (1993) 11 385.
[16] M.F. Rodríguez Prieto, B. Nickel, K.H. Grellmann, A. Mordziński, Chem. Phys. Lett. 146 (1988) 387.
[17] W. Al-Soufi, K.H. Grellmann, B. Nickel, J. Phys. Chem. 95 (1991) 10 503.
[18] H. Eisenberger, B. Nickel, A.A. Ruth, W. Al-Soufi, K.H. Grellmann, M. Novo, J. Phys. Chem. 95 (1991) 10 509.
[19] K.H. Grellmann, A. Mordziński, A. Heinrich, Chem. Phys. 136 (1989) 201.
[20] S.P. McGlynn, T. Azumi, M. Kinoshita, Molecular Spectroscopy of the Triplet State (Prentice-Hall, Englewood Cliffs, NJ, 1969).