

## Photoinduced Intramolecular Hydrogen Atom Transfer of *N*-Salicylideneaniline in the Triplet State

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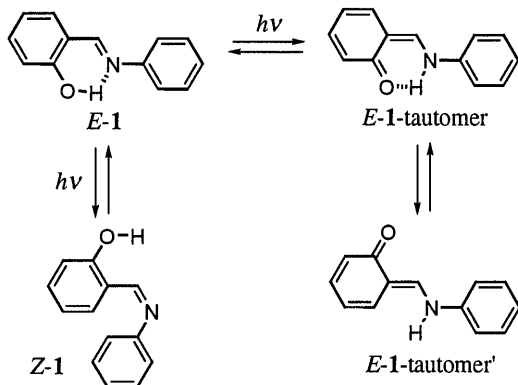
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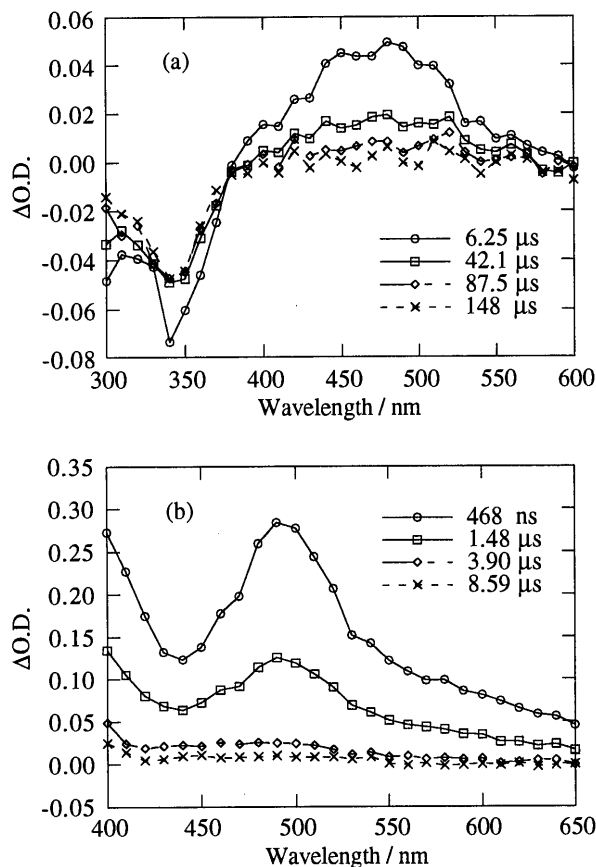
The excited triplet state of *N*-salicylideneanilines, benzyldeneaniline derivatives, was successfully observed for the first time due to the intramolecular hydrogen bonding by means of transient absorption spectroscopy in solution. And the adiabatic intramolecular hydrogen atom transfer in the triplet state is proposed.

Photochromism as well as thermochromism and solvatochromism of *N*-salicylideneanilines has extensively been studied. As to the photochromism some of them undergo intramolecular hydrogen atom transfer to give the tautomer with intramolecular hydrogen bonding in the excited singlet state followed by the deactivation to give the tautomer' without having intramolecular hydrogen bonding.<sup>1-4</sup> However, the properties of *N*-salicylideneanilines in the excited triplet state have scarcely been studied. Only the possibility of production of tautomer was theoretically predicted.<sup>5</sup> In this respect, we have studied the photochromic behavior of *N*-salicylideneanilines (**1**) in the excited triplet state.

On irradiation of **1** ( $4.0 \times 10^{-5}$  M,  $M = \text{mol dm}^{-3}$ ) in benzene with 308 nm laser light, the transient absorption spectrum with the absorption maximum at 480 nm was observed in addition to the bleaching at 350 nm (Figure 1a). Since the time profile of the transient spectrum was not affected by the presence of oxygen, the former was assigned to the tautomer produced by intramolecular hydrogen atom transfer in the excited state followed by isomerization to the ground state tautomer, *E*-1-tautomer'. The latter was assigned to the *E*-to-*Z* isomerization around the C=N double bond. Laser photolysis of benzyldeneaniline which has no intramolecular hydrogen bonding gave only the bleaching around 350 nm due to the *E*-to-*Z* isomerization<sup>6</sup> around the C=N double bond.



On biacetyl ( $E_T = 56.5 \text{ kcal mol}^{-1}$ ,  $\text{cal} = 4.184 \text{ J}$ )<sup>7</sup> sensitization, **1** gave the transient absorption spectra at 480 nm with the lifetime of  $1.5 \mu\text{s}$  in benzene (Figure 1b). The transient shown in Figure 1b was quenched by oxygen with the rate con-



**Figure 1.** (a) Transient absorption spectra of **1** ( $4.0 \times 10^{-5}$  M) on excitation at 308 nm and (b) transient absorption spectra of **1** ( $5.0 \times 10^{-3}$  M) sensitized with biacetyl ( $3.0 \times 10^{-2}$  M) on excitation at 425 nm under Ar in benzene.

stant of  $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which is ca. 1/9 of the diffusion controlled rate constant and was assigned to the triplet state of **1**. The energy transfer rate constant from the biacetyl triplet to **1** ( $k_q$ ) was determined by measuring the decay rate constant of biacetyl triplet at 320 nm in the presence of varying concentration of **1** with 425 nm laser excitation. Thus, the decay rate constant of biacetyl triplet in the presence or absence of **1** was determined to be  $1.43 \times 10^5$ ,  $1.82 \times 10^5$ ,  $2.5 \times 10^5$ , and  $5.0 \times 10^5 \text{ s}^{-1}$  for  $[\mathbf{1}] = 0$ ,  $5 \times 10^{-5}$ ,  $1.0 \times 10^{-4}$ , and  $2.0 \times 10^{-4}$  M, respectively in benzene. The plot of the observed decay rate constant vs the concentration of **1** gave the  $k_q$  value to be  $1.83 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

The rate constant of energy transfer from the biacetyl triplet to benzyldeneaniline was determined to be  $1.35 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  by the similar procedure as **1**. The observed  $k_q$  value for benzyldeneaniline is similar to that of **1**. However, the

absorption spectrum of benzylideneaniline triplet was not observed on biacetyl sensitization. Therefore, we can assume that the triplet state of benzylideneaniline does not have enough lifetime to be detected by ns laser flash photolysis.

In order to make clear the reason why the triplet lifetime of **1** is considerably longer than benzylideneaniline, we tried to determine the potential energy surfaces of triplet state by estimating the triplet energies of the starting form and the relaxed form.

As described above, the quenching rate constant of biacetyl triplet by **1** ( $k_q$ ) is less than half of the diffusion controlled rate constant, indicating that the energy transfer process is not fully exothermic process but is slightly endothermic process. By using the equation 1,<sup>8</sup> where  $\Delta E$  is the triplet energy difference between the biacetyl and **1** and  $k_{dif}$  is the diffusion controlled rate constant estimated to be  $6.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>9</sup> we can estimate  $\Delta E$  to be  $0.5 \text{ kcal mol}^{-1}$ . This value means that the energy transfer process from triplet biacetyl to **1** is  $0.5 \text{ kcal mol}^{-1}$  endothermic and therefore, the triplet energy of **1** is estimated to be ca.  $57 \text{ kcal mol}^{-1}$ .

$$k_q = k_{dif} \exp(-\Delta E_a / RT) / [1 + \exp(-\Delta E_a / RT)] \quad (1)$$

If the relaxed triplet produced by energy transfer process from biacetyl to **1** takes a conformation similar to that of the starting conformer *E-1*, the triplet state of **1** should have the energy of ca.  $57 \text{ kcal mol}^{-1}$  over the ground state. However, the triplet state of **1** was not quenched by trans-stilbene ( $E_T = 49.3 \text{ kcal mol}^{-1}$ )<sup>7</sup> which has much less triplet energy than  $57 \text{ kcal mol}^{-1}$ . In addition, although the triplet state of **1** was quenched by anthracene ( $E_T = 42.5 \text{ kcal mol}^{-1}$ ),<sup>7</sup> the quenching rate constant was lower than the diffusion controlled rate constant and was  $1.66 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . From this quenching rate constant and eq 1, one can estimate the relaxed triplet energy of **1** to be ca.  $42 \text{ kcal mol}^{-1}$ .

The difference of the triplet energies estimated from the two experiments indicates that the conformation of the relaxed triplet is very much different from that of the Frank-Condon triplet. Therefore, we will propose that the observed triplet state should be the tautomer, produced by the adiabatic intramolecular hydrogen atom transfer in the triplet state. The fact that the lifetime of the observed triplet state is considerably long may support the above proposition.

As to the deactivation processes from the triplet state, we have observed only the T-T absorption spectrum but the ground state tautomer was not observed on triplet sensitization in benzene. Therefore, the deactivation from the tautomer triplet gives only the ground state tautomer (*E-1*-tautomer) which quickly reverts to the ground state starting conformer *E-1*. However, on direct irradiation we observed a tautomer ground state which is produced by intramolecular hydrogen atom transfer in the excited singlet state followed by deactivation with isomerization around the double bond to *E-1*-tautomer'. Based on these results we will propose the potential energy diagram of hydrogen atom transfer in the excited triplet state as well as singlet states as shown in Figure 2.

Much work has been focused on the singlet state photochromism in *N*-salicylideneanilines (**1**). However, our find-

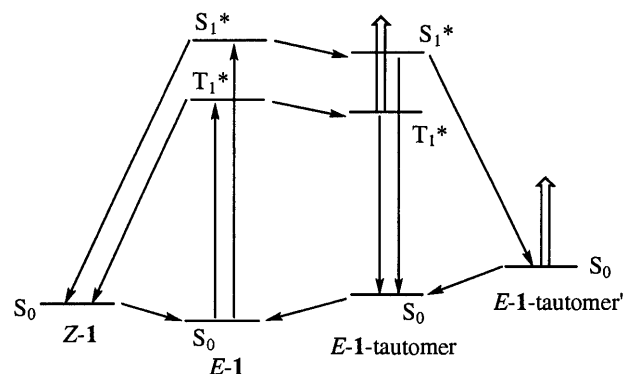


Figure 2. Potential energy diagram of **1** in benzene.

ing clearly shows that the hydrogen atom transfer could also take place in the triplet state to give the tautomer as an adiabatic process. To the best of our knowledge, this is the first clear observation of the triplet state of benzylideneaniline derivatives by introduction of the hydroxy group capable to form intramolecular hydrogen bonding and to induce intramolecular hydrogen atom transfer.

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- K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964).
- Y. Norikane and T. Arai, *Chem. Lett.*, **1999**, 909. The decay curve of the absorption spectrum of the benzophenone triplet ( $E_T = 68.6 \text{ kcal mol}^{-1}$ ) in benzene was monitored at 530 nm in the presence or absence of naphthalene ( $E_T = 60.5 \text{ kcal mol}^{-1}$ )<sup>7</sup> as a quencher. The plot of the decay rate constant of the benzophenone triplet vs the concentration of naphthalene gave the quenching rate constant to be  $6.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and therefore we estimated the  $k_{dif}$  value to be  $6.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .