Novel Insight into the Photochromism and Thermochromism of Hydrogen Bonded Schiff Bases

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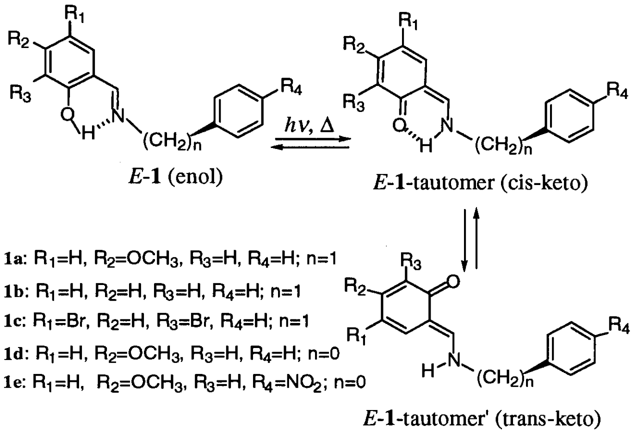
The equilibrium between the enol form and the keto form in the triplet state of salicylideneanilines and salicylidenebenzylamines **1** in non-polar solvent has been explored based on the observation of phosphorescence and T–T absorption spectra.

Photochromism and thermochromism have been extensively studied for aromatic Shiff bases in the form of crystal.[1,2] For example, Oohashi et al. studied the structural change upon photoirradiation of the crystal of *N*-3,5-di-*tert*-butylsalicylidene-3-nitroaniline and determined the structure of the photoinduced colored species as the trans-keto form.[3] Ogawa et al. reported the temperature dependent crystal structure change of *N*-(5-chloro-2-hydroxybenzylidene)-4-hydroxyaniline, where the population of the enol form decreased with the concomitant increase of the cis-keto form with decreasing of temperature.[4] However, little effort has been directed towards revealing the triplet state behaviors of aromatic Shiff bases. Actually, we could not find the report for the observation of phosphorescence spectra in aromatic Shiff bases. This must be the reason for the lack of information for the triplet state behaviors of Shiff bases. We wish to report here the observation of the phosphorescence spectra for the first time in salicylideneanilines and salicylidenebenzylamines. Thus, **1a**–**1e** exhibited phosphorescence spectra and the triplet state behaviors of **1** were elucidated.

The absorption spectrum of *E*-**1a** showed a long-wavelength onset near 350 nm with maxima at 315 and 280 nm in methylcyclohexane at room temperature. The fluorescence as well as the phosphorescence spectrum was not observed at room temperature. With lowering of temperature, the absorption spectra shifted to the longer wavelength with a long-absorption onset at 420 nm and maxima at 370 and 295 nm.[5,6] The fluorescence spectrum was observed with a maximum at 450 nm at 77 K which is similar to the spectrum reported.[5] The compounds **1b**–**1e** exhibited similar fluorescence and absorption properties.



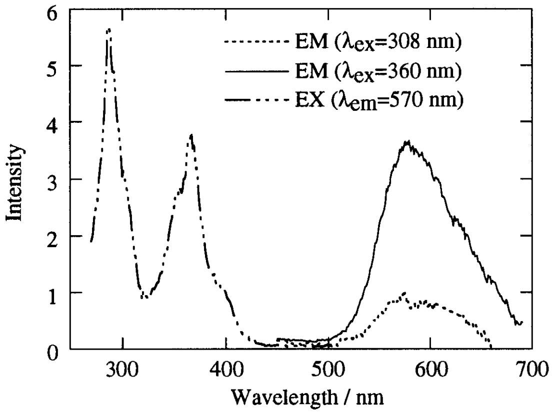


Figure 1. Phosphorescence spectra of **1a** (4.0×10^{-5} M) in methylcyclohexane at 77 K.

Figure 1 shows phosphorescence spectra observed for *E*-**1a** with a maximum at 577 nm at 77 K. The onset of the phosphorescence spectrum appeared at 510 nm and one can estimate the triplet energy of *E*-**1a** to be 56 kcal mol^{-1}. The phosphorescence spectra were also observed for **1b**–**1e** with the phosphorescence maximum at 568–600 nm and the onset at 510–535 nm. Thus, the triplet energies of these Schiff bases **1b**-**1e** were estimated to be 53.5–56 kcal mol^{-1}.

As described above, the absorption spectrum at 77 K indicates that **1a** exists mainly as the *E*-**1a**-tautomer at 77 K. In addition, the phosphorescence excitation spectrum can be superimposed on the absorption spectrum of *E*-**1a**-tautomer. Therefore, the light is absorbed by *E*-**1a**-tautomer at 77 K followed by intersystem crossing to the triplet state. It seems likely that the phosphorescence was emitted from the *E*-**1a**-tautomer, but as described later it might be emitted from *E*-**1a** after reverse hydrogen atom transfer in the excited triplet state.

In order to study the above mentioned structure of the triplet state, we have determined the triplet energy of *E*-**1a** in benzene at room temperature by laser flash photolysis experiments.

On irradiation of **1a** in benzene with 308 nm laser light, the transient absorption spectra with the absorption maximum at 430 nm was observed (Figure 2a). The time profile of the transient spectra was not affected by oxygen and the transient was assigned to the ground state, most probably the tautomer produced by intramolecular hydrogen atom transfer in the excited singlet state followed by isomerization to the ground state tautomer, *E*-**1a**-tautomer.[7]

On biacetyl (E_T = 56.5 kcal mol^{-1})[8] sensitization, *E*-**1a** gave the triplet-triplet (T–T) absorption spectra at 430 nm with the lifetime of 2.2 μs in benzene (Figure 2b). Although the absorption maximum observed by sensitization is almost the same with that observed on direct irradiation, the transient

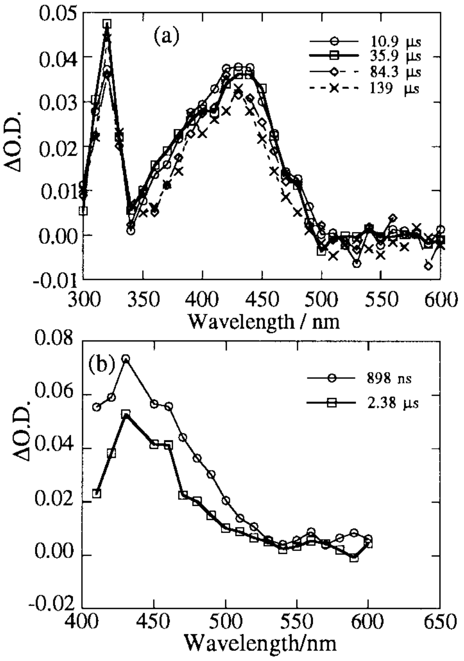


Figure 2. (a) Transient absorption spectra of **1a** (4.0×10^{-5} M) on exciation at 308 nm and (b) T–T absorption spectra of **1a** (5.0×10^{-3} M) sensitized with biacetyl (3.0×10^{-2} M) on excitation at 425 nm under Ar in benzene.

absorption spectrum observed on triplet sensitization was quenched by molecular oxygen with the rate constant of 2×10^9 M^{-1} s^{-1}, which is the usual value of the quenching rate constant for the triplet state by oxygen and the transient is assigned to the triplet state.

The energy transfer rate constant from the biacetyl triplet to *E*-**1a** was determined by measuring the decay rate constant of biacetyl triplet in the presence of varying concentration of *E*-**1a** with 425 nm laser excitation. The rate constant thus determined is 1.9×10^8 M^{-1} s^{-1} and is less than half of the diffusion controlled rate constant, indicating that the energy transfer process is slightly endothermic process. By using the equation 1,[9] where ΔEa is the triplet energy difference between the biacetyl and *E*-**1a** and k_{dif} is the diffusion controlled rate constant estimated to be 6.3×10^9 M^{-1} s^{-1},[7] we can estimate ΔE_a to be 2 kcal mol^{-1}. Thus, the energy transfer process from triplet biacetyl to *E*-**1a** is 2 kcal mol^{-1} endothermic and the triplet energy of *E*-**1a** is estimated to be 58.5 kcal mol^{-1}.

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

On the other hand, the triplet state of *E*-**1a** was not quenched by *trans*-stilbene (E_T = 49.3 kcal mol^{-1})[8] which has much less triplet energy than 58.5 kcal mol^{-1}. In addition, although the triplet state of *E*-**1a** was quenched by anthracene (E_T = 42.5 kcal mol^{-1}),[8] the quenching rate constant was lower than the diffusion controlled rate constant and was 2.9×10^8 M^{-1} s^{-1}. From this quenching rate constant and eq. 1, one can estimate the relaxed triplet energy of *E*-**1a** to be 40.8 kcal mol^{-1}.

The difference of the triplet energies estimated from the two experiments indicates that the observed triplet state at room temperature should be *E*-**1a**-tautomer, produced by the intramolecular hydrogen atom transfer in the triplet state (Figure 3).

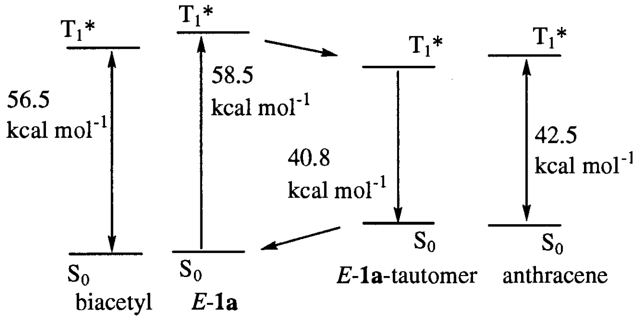


Figure 3. Potential energy diagram of **1a**, sensitizer biacetyl, and quencher anthracene at room temperature in benzene.

Since the triplet energy determined from the phosphorescence spectrum at 77 K, 56 kcal mol^{-1}, is very much different from the triplet energy of the relaxed state (*E*-**1a**-tautomer, keto form) (40.8 kcal mol^{-1}) but is close to that of the enol form (58.5 kcal mol^{-1}) at room temperature, the phosphorescent state should have a structure very much similar to the enol form (*E*-**1a**). Although the *E*-**1a**-tautomer is populated in the ground state and the light is absorbed by the tautomer, it might facilely undergo reverse hydrogen atom transfer to give the enol form *E*-**1a** as an adiabatic process in the triplet state.

The similar experiments indicated the occurence of the hydrogen atom transfer in the excited triplet state of **1b**–**1e** at room temperature. In addition, the phosphorescence spectra of **1b**–**1e** could also be assigned to the enol form.

In summary, *E*-**1** underwent adiabatic hydrogen atom transfer to give the tautomer in the excited triplet state at room temperature. However, the colored form (keto form) which is more stable in the ground state glassy matrix of methylcyclohexane seems to undergo reverse hydrogen atom transfer to give the enol form in the excited triplet state at 77 K.

To the best of our knowledge, this is the first clear observation of the phosphorescence spectra for salicylideneanilines and salicylidenebenzylamines.

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