Substituent Effects on the Zero-field Splitting Constants for the Triplet Ketoamines Generated by Excited State Intramolecular Proton Transfer in Schiff Bases

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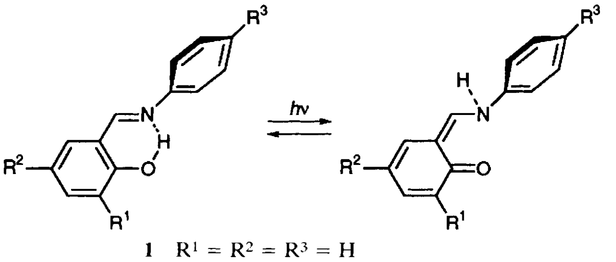
Time-resolved EPR spectra have been measured for the short-lived excited triplet states of the ketoamine tautomers generated by excited state intramolecular proton transfer reaction in Schiff bases.

Aromatic Schiff bases have been of interest for more than three decades because of their photochromic properties.[1,2] The photochromism of salicylideneaniline derivatives was established by excited state intramolecular proton transfer (ESIPT). The number of kinetic studies on ESIPT reactions has increased in recent years.[3–5] Photoinduced intramolecular proton transfer generally takes place in the excited singlet state of the enol–imine form on the picosecond time scale, generating the excited twisted zwitterion. The zwitterion subsequently isomerizes to the excited singlet state of the *trans*-ketoamine tautomer. The excited triplet ketoamine should be generated during the relaxation process,[6,7] but non-existent or very weak phosphorescence has prevented studies of the electronic structure and properties. It is noteworthy that no T-T absorption spectrum was measured for free Schiff base systems by laser photolysis techniques at room temperature.[5] We now report substituent effects on the electronic structure of the short-lived triplet states of the ketoamine tautomers. The Schiff bases investigated are shown in Fig. 1.

Salicylideneaniline **1** was purchased from Tokyo Kasei and purified by recrystallization from methanol. The imines **2**–**4** were prepared from the corresponding salicylaldehydes and anilines, and then purified by distillation or recrystallization. The solvent, toluene, was of spectroscopic grade. Time-resolved EPR (TREPR) spectroscopic studies were carried out as described previously.[8] An excimer laser (Lumonics HE-400, XeCl 308 nm) and a Nd:YAG laser (Quanta-Ray GCR-14S, 355 nm) were used as the light source. Emission spectra were measured with an Hitachi 850 fluorescence spectrometer. The sample solutions for TREPR and emission measurements had concentrations of 1×10^{-3} and 5×10^{-5} mol dm^{-3}, respectively.

Fig. 2 shows emission and excitation spectra of the free Schiff bases **2**–**4** in a toluene glassy matrix at 77 K. No phosphorescence was observed for the present systems. Large Stokes-shifted fluorescence spectra were observed indicating the occurrence of ESIPT. The fluorescence spectrum of **2**, with maxima at 520 and 553 nm, is similar to that of the parent anil **1** (λ = 525 and 550 nm). On the other hand, a red-shifted fluorescence with maxima at 554 and 593 nm was observed for **3**. The blue-shifted fluorescence with one peak at 505 nm for **4** is in good agreement with that reported previously.[5] The excitation spectra were almost identical to those of the corresponding absorption spectra.



1 $R^1 = R^2 = R^3 = H$
2 $R^1 = R^2 = H$, $R^3 = Ac$
3 $R^1 = R^2 = Br$, $R^3 = Ac$
4 $R^1 = H$, $R^2 = NO_2$, $R^3 = Ac$

Fig. 1 Molecular structures of enol–imine and ketoamine tautomers of Schiff bases

Fig. 3 shows the observed and simulated TREPR spectra generated by laser photolysis of the present Schiff bases in a toluene glassy matrix at 77 K. Observation of the $\Delta M_S = \pm 2$ transitions at 0.155–0.16 T clearly indicates the generation of the transient triplet species during the relaxation process. No signal due to the triplet state was detected by using a conventional EPR spectrometer with 100 kHz field modulation. For **1**–**3**, excitations with both the excimer (308 nm) and the Nd:YAG (355 nm) lasers gave the same triplet TREPR spectra. However, only a very weak and unanalysable TREPR spectrum was obtained in the photolysis of **4** with 308 nm light. This is probably due to the efficient photochromism reaction and to very slow back proton transfer. We observed the transient triplet spectrum by the excitation of **4** with 355 nm light.

Notable substituent effects on the zero-field splitting (ZFS) parameters and intersystem crossing (ISC) selectivity were observed. The EPR data determined by computer simulation are summarized in Table 1. The order of the triplet sublevels

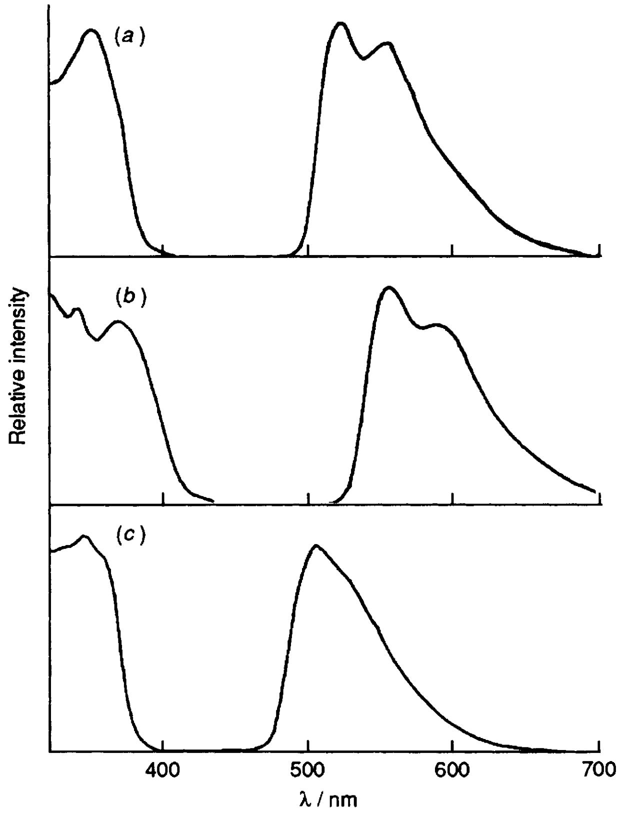


Fig. 2 Emission (uncorrected) and excitation spectra of (*a*) **2**, (*b*) **3** and (*c*) **4** in a toluene glassy matrix at 77 K. The excitation wavelength is 380 nm and monitor wavelengths are 520, 540 and 500 nm for **2**, **3** and **4**, respectively.

was tentatively assigned as in-plane T_x and T_y, and out-of-plane T_z. It can be considered that the directions of the in-plane principal axes are slightly different in these triplet states. The $|D|$ values obtained from **1** and **2** are very small compared with those of normal aromatic $^3\pi\pi^*$ states but similar to those of the triplet ketoamines of the other free Schiff bases,[6,7] and of the triplet photoenols of *o*-hydroxyacetophenone[9] and *o*-methylacetophenone.[10,11] These enols have similar π systems with 1,4-diradical character. Therefore, the transient EPR spectra are assigned to the triplet ketoamine forms generated from ESIPT reactions.

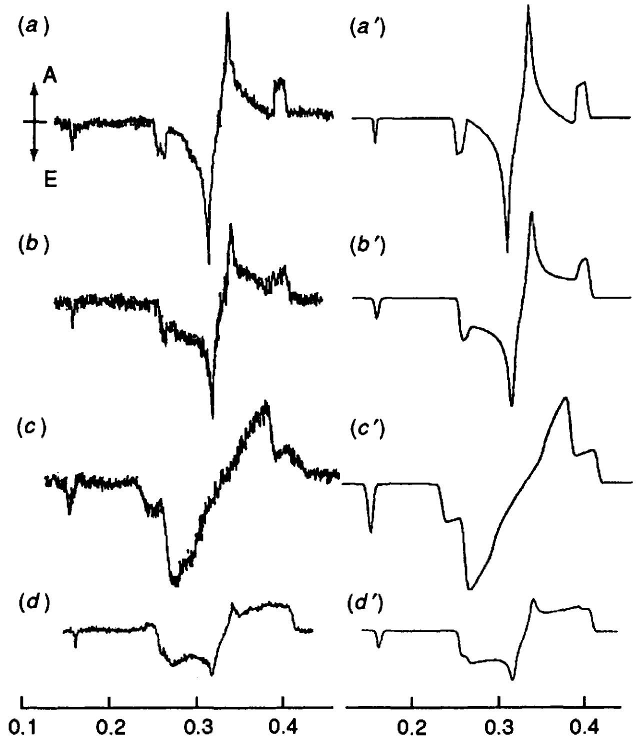


Fig. 3 Observed (*a–d*) and simulated (*a'–d'*) TREPR spectra of the triplet ketoamines generated by laser photolysis of (*a*) **1**, (*b*) **2**, (*c*) **3** and (*d*) **4** in a toluene glassy matrix at 77 K. The spectra were observed 1 μs after the laser pulse. The excitation wavelengths are 308 nm for **1–3** and 355 nm for **4**, respectively.

Table 1 Zero-field splitting parameters and relative population (p) in the zero-field sublevels for the triplet ketoamines generated by excited state intramolecular proton transfer in Schiff bases

Sample	$\|D\|/\text{cm}^{-1}$	$\|E\|/\text{cm}^{-1}$	p_x	p_y	p_z
1	0.068	0.019	0.00	1.00	0.0
2	0.070	0.016	0.25	0.75	0.0
3	0.085	0.010	0.67	0.33	0.0
4	0.073	0.017	0.40	0.60	0.0

The observed spin polarization pattern EEAE/AEA for **1** indicates preferential population of the middle T_y sublevel, where E and A denote emission and enhanced absorption of the microwave, respectively. The acetyl substituent of the phenyl group in **2** induces small changes in the ZFS parameters but a distinct change for the ISC selectivity. On the other hand, for **3** the ZFS parameters and the spectral pattern are quite different from those for **1** and **2**. Except for the red-shift of the absorption and emission spectra for **3**, the photochromic behaviour is very similar in these Schiff bases. Thus, we assigned the TREPR spectrum observed for **3** as due to the triplet ketoamine tautomer. The heavy bromine atom would induce a change in mixing character of the higher excited states to the T_1 state. In the nitro derivative **4**, the relative ISC populating rates for the highest and middle sublevels were 0.40 and 0.60, respectively. It is clear from Table 1 that the electron attractive nitro group affects the ISC selectivity but has little influence on the ZFS parameters.

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