

## Time-resolved E.S.R. Study of Triplet Ketoamines Generated by Intramolecular Proton Transfer in Free Schiff Bases

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Non-phosphorescent triplet states of the ketoamine forms of several free Schiff bases generated by intramolecular proton transfer have been observed using a time-resolved e.s.r. method.

Much attention has been given to the intramolecular proton transfer reactions of molecules in excited states.<sup>1-3</sup> In particular, the photochromism of salicylideneimine (Sal) derivatives (free Schiff bases) has been extensively investigated (Scheme 1). Recent work<sup>4,5</sup> has established that proton transfer from the  $S_1$  state of the enolimine yields vibrationally excited ketoamine, which produces the photochromic *trans*-ketoamine and the  $S_1$  state of the *cis*-isomer. The triplet ( $T_1$ ) state of the ketoamine should be generated during the process, but its non-phosphorescence has prevented study of its electronic structure. In the present work, we detected the  $T_1$  state of the ketoamine in a glassy matrix using a time-resolved e.s.r. technique.

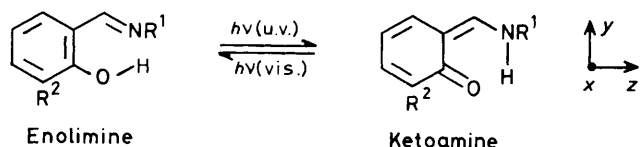
Transient e.s.r. spectra were measured using a JEOL FE2XG X-band e.s.r. spectrometer modified for a wide-band preamplifier without magnetic modulation. The e.s.r. signal was passed through a boxcar integrator (PAR 162) at arbitrary times after the laser pulse. A nitrogen laser (Molelectron UV-24, 337 nm) was used as the light source. Samples (1)–(4)

(Table 1) were prepared from the corresponding salicylaldehydes and the appropriate amines and then purified by distillation under low pressure or recrystallization.

Figure 1a shows the time-resolved e.s.r. spectrum observed for (2) in a toluene glassy matrix 1  $\mu$ s after the laser pulse. The emission signal at about 0.155 T is the  $|\Delta M_S| = 2$  transition. The spin polarization of the  $|\Delta M_S| = 1$  transition is EAE in the low field half and AEA in the high field half, where A and E denote enhanced absorption and emission of microwave radiation, respectively. The zero-field splitting (ZFS) parameters  $|D| = 0.074$  and  $|E| = 0.015$  cm<sup>-1</sup> were obtained from the spectrum (Table 1). These values are completely different from those of the corresponding Zn complex.<sup>6</sup>

The transient e.s.r. spectrum observed for (1) was very similar to that of (2). Measurements were also made for (3) and (4) (Figure 1b and c, respectively) in order to clarify the substituent effect on the ZFS parameters. Similar polarization patterns were observed though smaller ZFS values were obtained (Table 1). The reduction in the ZFS parameters caused by substitution by a phenyl moiety at nitrogen and a methoxy group at the 3-position may be ascribed to the delocalization of unpaired spins. No conventional e.s.r. signal due to the triplet state was detected during continuous irradiation of (1)–(4) under the same conditions.

The observed transient e.s.r. spectra may be assigned to the  $T_1$  ( $^3\pi\pi^*$ ) state of ketoamines generated by intramolecular proton transfer for the following reasons. The very large



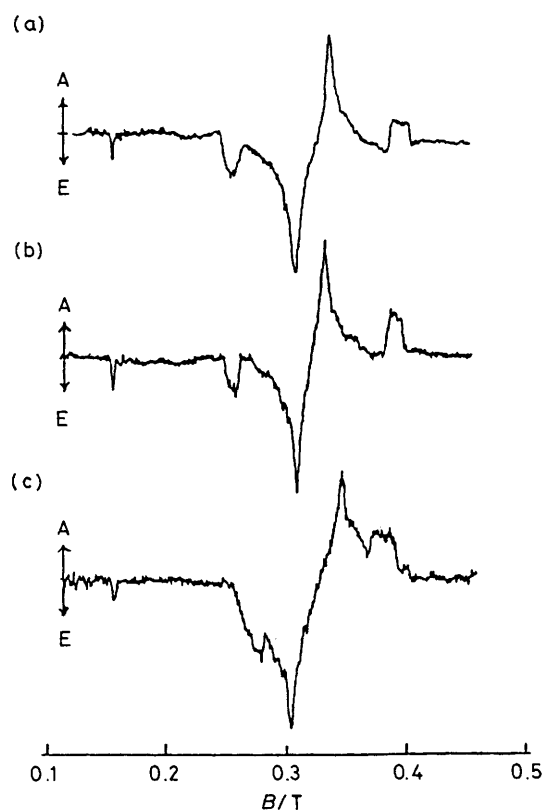
Scheme 1

**Table 1.** Zero-field splitting parameters for the triplet ketoamines generated by intramolecular proton transfer in free Schiff bases.

Sample	R <sup>1</sup>	R <sup>2</sup>	$ D /\text{cm}^{-1}$	$ E /\text{cm}^{-1}$
(1) Salicylideneimine	H	H	0.073	0.015
(2) <i>N</i> -Methylsalicylideneimine	Me	H	0.074	0.015
(3) <i>N,N'</i> -( <i>o</i> -Phenylene)bis(salicylideneimine)	C <sub>6</sub> H <sub>4</sub> -Sal	H	0.070	0.014
(4) <i>N</i> -Methyl-3-methoxysalicylideneimine	Me	OMe	0.064	0.006

**Table 2.** Electron spin polarization pattern and ZFS parameters for the intermediate triplet species generated by tautomeric isomerization of free Schiff base (2), OHAP, and OMAP.

	(2)	OHAP <sup>8</sup>	OMAP <sup>9</sup>
Spin polarization	EEAE/AEA	EEAE/AEA	EAEA/EAE
$ D /\text{cm}^{-1}$	0.074	0.073	0.060
$ E /\text{cm}^{-1}$	0.015	0.013	0.003
Precursor	S <sub>1</sub>	S <sub>1</sub>	T <sub>1</sub>



**Figure 1.** Time-resolved e.s.r. spectra of the triplet ketoamines generated by laser pulse irradiation of (a) (2), (b) (3), and (c) (4) in a toluene glassy matrix at 77 K. The spectra were observed 1  $\mu$ s after the laser pulse.

Stokes shift of fluorescence in the present systems suggests the formation of ketoamines on u.v.-irradiation of the S<sub>1</sub> state of the enolimes. The T<sub>1</sub> state of the parent enolimes may be expected to be the <sup>3</sup>nπ\* state, with larger  $|D|$  values than ours, by analogy with 2-phenylpyrroline, for which Sotoyama and Azumi<sup>7</sup> obtained a  $|D|$  value of 0.20 cm<sup>-1</sup> and observed preferential intersystem crossing (ISC) to the highest triplet sublevel. Furthermore, the ZFS values obtained in the present systems were close to those of the triplet photoenols produced from *o*-hydroxyacetophenone (OHAP)<sup>8</sup> and *o*-methylacetophenone (OMAP),<sup>9</sup> as shown in Table 2. These enols have very similar π systems.

The spin polarization patterns observed in the present systems are the same as that of OHAP. This is probably attributable to the similarity of the tautomeric isomerization

mechanisms. In free Schiff bases and OHAP the isomerization is induced *via* intramolecular proton transfer from the S<sub>1</sub> states, while it occurs *via* hydrogen atom transfer from the T<sub>1</sub> state in OMAP. The order of the triplet sublevels was tentatively assigned as T<sub>z</sub>, T<sub>y</sub>, and out-of-plane T<sub>x</sub>, by analogy with OHAP.<sup>8</sup> The observed spin polarization pattern EEAE/AEA suggests preferential population of the middle T<sub>y</sub> sublevel.

The ZFS parameters obtained for the triplet ketoamines are very small compared with those of the corresponding Zn complexes, *i.e.*  $D = 0.074 \text{ cm}^{-1}$  for (2),  $0.0930 \text{ cm}^{-1}$  for Zn(Sal-N-Me)<sub>2</sub>,  $0.071 \text{ cm}^{-1}$  for (3), and  $0.0826 \text{ cm}^{-1}$  for Zn(Salophen). Semiempirical calculations suggest that the unpaired spins are localized on one salicylideneimino ligand in Zn(Sal-N-Me)<sub>2</sub>, while in the planar Zn(Salophen) the spins are delocalized over the molecular framework.<sup>6</sup> The π framework of (2) is thus very similar to that of its Zn complex. It is clear that in (3) there is little delocalization of the spins in the phenyl and in other salicylideneimino groups because of their nonplanarity. The small  $|D|$  values in the present systems are probably due to the change in mixing character of the higher excited states to the very low energy T<sub>1</sub> state. There is no data on the energy level of the triplet ketoamines owing to their non-phosphorescence. For the triplet enol of OMAP,  $E(T_1) \approx 25 \text{ kcal mol}^{-1}$  was estimated from a T-T energy transfer experiment,<sup>10</sup> a similar energy level might be expected for the triplet ketoamine.

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## References

- W. Klopffer, *Adv. Photochem.*, 1977, **10**, 311.
- D. Huppert, M. Gutman, and K. J. Kaufmann, *Adv. Phys. Chem.*, 1981, **47**, 643.
- E. M. Kosower and D. Huppert, *Ann. Rev. Phys. Chem.*, 1986, **37**, 127.
- R. Nakagaki, T. Kobayashi, J. Nakamura, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1909.
- P. F. Barbara, P. M. Rentzepis, and L. E. Brus, *J. Am. Chem. Soc.*, 1980, **102**, 2786.
- S. Tero-Kubota, K. Migita, H. Oshio, and J. Higuchi, 'Electronic Magnetic Resonance of the Solid State,' ed. J. A. Weil, Canadian Society for Chemistry, Ottawa, Canada, 1987, p. 619.
- W. Sotoyama and T. Azumi, personal communication.
- S. Yamauchi and N. Hirota, *J. Am. Chem. Soc.*, 1988, **110**, 1346.
- K. Akiyama, Y. Ikegami, and S. Tero-Kubota, *J. Am. Chem. Soc.*, 1987, **109**, 2538.
- C. V. Kumar, S. K. Chattopadhyay, and P. K. Das, *J. Am. Chem. Soc.*, 1983, **105**, 5143.