

Excited Triplet State Generated from Excited State Intramolecular Proton Transfer in 2-(2'-Hydroxyphenyl)benzothiazole

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The short-lived triplet state of the keto tautomer of 2-(2'-hydroxyphenyl)benzothiazole generated by excited state intramolecular proton transfer has been measured using a time-resolved electron paramagnetic resonance method.

The technique of time-resolved electron paramagnetic resonance (EPR) has played an important role in proving the generation of excited triplet (T_1) states during the relaxation process in photoinduced intramolecular hydrogen or proton transfer reactions.¹⁻⁷ Recently, it has been suggested for the 2-(2'-hydroxyphenyl)benzothiazole (HBT) system that the transient absorption ($\lambda_{\max} = 500$ nm in 3-methylpentane)⁸ and

the phosphorescence ($\lambda_{\max} = 648$ nm in methylcyclohexane)⁹ spectra are due to the T_1 state of the *cis*-keto tautomer (*cis*- 3K) produced from the excited state intramolecular proton transfer (ESIPT). Temperature dependence of the transient absorption and the delayed fluorescence suggest that the enol triplet state (3E) of HBT lies in energy terms above the *cis*- 3K . The yield of the 3E from the 1E in HBT is

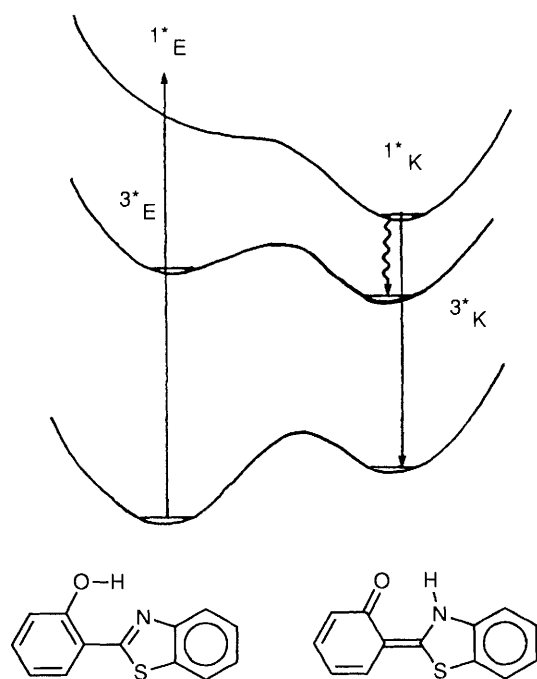


Fig. 1 Schematic energy diagram of the ground and excited states of 2-(2'-hydroxyphenyl)benzothiazole

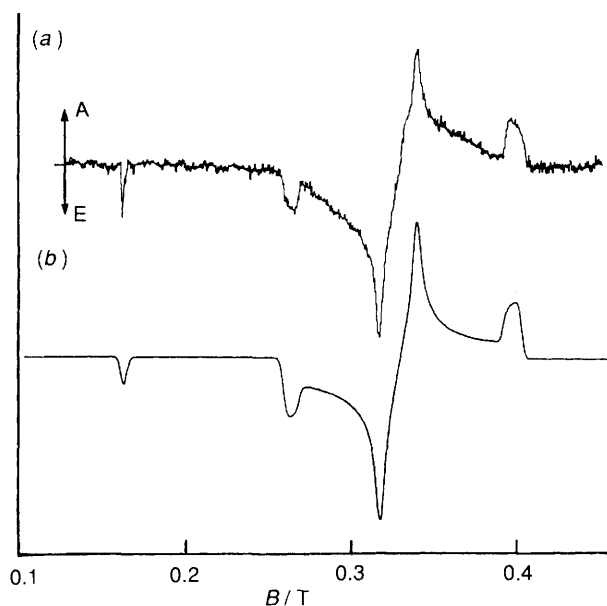


Fig. 2 (a) Observed and (b) simulated time-resolved EPR spectra of triplet *cis*-keto tautomer of 2-(2'-hydroxyphenyl)benzothiazole in a toluene glassy matrix. The observed spectrum was taken 1 μ s after the laser pulse (308 nm) at 77 K.

negligible, as the ES IPT rate is very fast: 170 ± 20 fs in C_2Cl_4 .¹⁰ The *trans*-K tautomer cannot be produced at low temperature.^{11,12} Therefore, the energy levels in the HBT system are as shown in Fig. 1. In the present paper, we measured the EPR spectra of the T_1 states of HBT and related molecules, 2-phenylbenzothiazole (PBT), 2-(2'-hydroxyphenyl)benzoxazole (HBO), and 2-(2'-hydroxy-5'-methylphenyl)benzotriazole in a glassy matrix.

All of the substances were purified by recrystallization from appropriate solvents. The sample solution prepared at a concentration of 10^{-2} mol dm^{-3} was deoxygenated by argon gas bubbling. Measurements of time-resolved EPR spectra were carried out using a Varian X-band EPR spectrometer without magnetic field modulation. The transient EPR signal was taken into a box-car integrator (NF BX-531) at arbitrary

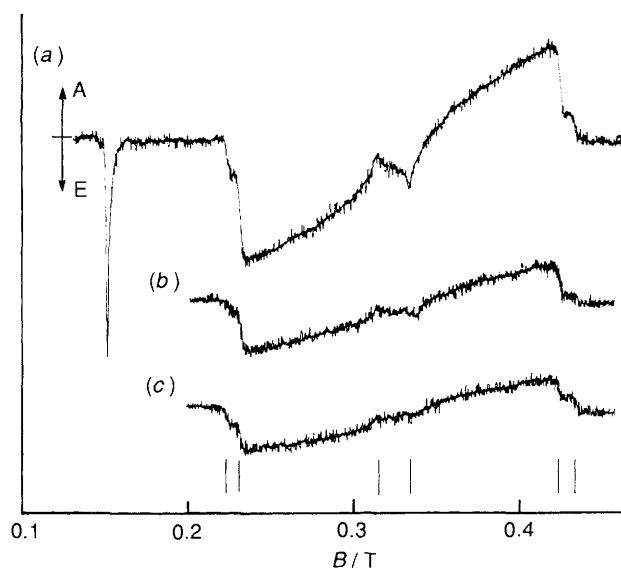


Fig. 3 Time-resolved EPR spectra of the T_1 state of phenylbenzothiazole in a toluene glassy matrix excited with (a) unpolarized light and (b) with polarized light parallel to B and (c) perpendicular to B . The spectra were observed 1 μ s after the laser pulse (308 nm) at 77 K. The bar indicates the canonical points.

times after the laser pulse. An excimer laser (Lumonics HE-400, XeCl 308 nm) was used as the light source.

Fig. 2(a) shows the time-resolved EPR spectrum obtained from the excimer laser irradiation (308 nm) of HBT in a toluene glassy matrix at 77 K. The spectrum was observed 1 μ s after the laser pulse. The $|\Delta M_S| = 2$ transition with emissive polarization was observed at 0.16 T. The polarization pattern of $|\Delta M_S| = 1$ transition is EAE/AEA, where E and A denote emission and enhanced absorption of the microwave, respectively. The zero-field splitting (ZFS) parameters $|D| = 0.069$ cm^{-1} and $|E| = 0.016$ cm^{-1} were determined from the spectral simulation [Fig. 2(b)]. The observed polarization pattern and ZFS parameters are very similar to those of the triplet *o*-quinoid tautomers generated from the ES IPT in Schiff bases,³ *o*-hydroxyacetophenone⁴ and *o*-aminoacetophenone.⁵ No conventional EPR signal was observed in this system under irradiation from an excimer laser and a high-pressure Hg lamp (500 W).

The T_1 state of PBT was also measured in a toluene glassy matrix, as the electronic structure would be expected to be similar to the enol tautomer of HBT. The transient EPR spectrum due to the T_1 state was clearly observed as shown in Fig. 3(a). The observed polarization pattern and the ZFS parameters ($|D| = 0.099$ cm^{-1} and $|E| = 0.027$ cm^{-1}) were entirely different from those of HBT. Magnetophotoselection measurements were carried out to discriminate the directions of out-of-plane and in-plane principal axes. Fig. 3(b) and (c) show the time resolved EPR spectra of the T_1 state of PBT excited with polarized light. The relative signal intensity of the outermost pair, which increased in the $\pi\pi^*$ excitation with the excitation light parallel to B , correspond to those from the molecules aligned with their molecular planes normal to B . The directions of in-plane principal axes are unclear for the present.

On the basis of these results, the T_1 state observed by the photolysis of HBT can be assigned to the *cis*- 3^*K ($3^*\pi\pi^*$) produced through intersystem crossing (ISC) from the 1^*K ($\pi\pi^*$) after ES IPT. It can be considered that the unpaired electrons in the *cis*- 3^*K ($\pi\pi^*$) mainly populate the *o*-quinoid moiety, as the ZFS parameters are close to those of the intermediate triplet species generated by tautomeric isomerizations.¹⁻⁷ Direct spin-orbit coupling between 1^*K ($\pi\pi^*$) and

${}^3K(\pi\pi^*)$ is unimportant and the vibronically coupled ${}^3n\pi^*$ state might be effective in the ISC process. The electron spin polarization of E EAE/AEA indicates that the preferential population occurs at the middle sublevel during the ISC process. Therefore, the direction of one of the in-plane principal axes may be close to the carbonyl bond of the *cis*-K tautomer.

We also attempted to measure the T_1 state of HBO. Laser photolysis of HBO gave two types of triplet EPR signals in a toluene glassy matrix, which are presumably assigned to the 3K and 3E tautomers. The observed spectral pattern and ZFS parameters ($|D| = 0.072 \text{ cm}^{-1}$ and $|E| = 0.014 \text{ cm}^{-1}$) of 3K are very similar to those of *cis*- 3K of HBT. Another, 3E , shows a broad spectral feature and has the ZFS value [$D^* = (D^2 + 3E^2)^{1/2} \text{ ca. } 0.11 \text{ cm}^{-1}$] corresponding to that of the usual ${}^3\pi\pi^*$ states. The 3E tautomer is considered to be produced by an equilibrium reaction between the tautomeric triplet states, as these two states are isoenergetic.^{13,14} On the other hand, no transient EPR signal was obtained from the laser irradiation of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole. This is probably because the quinoid form is unfavourable in this molecule.¹⁵

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