Nodal-plane model for excited-state intramolecular proton transfer of o-hydroxybenzaldehyde: substituent effect

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Abstract

The excited-state intramolecular proton transfer (ESIPT) of o-hydroxybenzaldehyde (OHBA) and related molecules in solution has been studied by emission spectroscopy. The substituent effects on the fluorescence quantum yield for the lowest excited 1 (π, π*) state can be explained by considering the nodal pattern of the wave function along with the delocalization of the π electrons in the excited state. The substituent effect in 5-substituted salicylaldehydes is much less than that in o-(substituted-formyl)phenols.

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1. Introduction

Much attention has been directed, from both experimental and theoretical viewpoints, toward the excited-state intramolecular proton transfer (ESIPT) of hydrogen-bonded molecules [1–12]. ESIPT is a very simple chemical process readily accessible for both accurate measurement and quantitative theoretical analysis. The study of ESIPT is at the forefront of the revolution in understanding chemical reactions at the molecular level.

We have investigated the dynamic processes in the low-lying excited states of o-hydroxybenzaldehyde (OHBA) and its related molecules (OHBAs) by using spectroscopic and computational methods [13–29]. We constructed a simple theoretical model of ESIPT in OHBAs, based on the nodal pattern of the wave function [17,18]. Although this nodal-plane model is qualitative, it allows us to immediately recognize the important features of ESIPT, and it provides useful information about the reaction mechanisms of ESIPT. Our model is applicable to various photochemical reactions occurring at various excited states of various molecules [30,31].

Many chemists have cited our nodal-plane model [5–12, 32–59], and recognized the usefulness of our explanation as mentioned below. Recent reviews [5,8–11,32] and special issues [6,7,12] have extensively discussed it. The mechanism of ESIPT for the lowest excited singlet state (S1 state) of 2,5-bis(benzoxazolyl)hydroquinone, in which only one proton is transferred even though the molecule has two equivalent intramolecular-hydrogen-bonds, has been explained in terms of our nodal-plane model [33,36,39]. The absence of proton transfer in the S1 state of 2-hydroxyquinoline has been understood in terms of nodal-plane analysis of the wave function [38]. The ESIPT’s of methylsalicylate (MS) [40], 2-hydroxy-3-naphthoate [42], salicylic acid (SA) [45] and hydroxyanthraquinones [48] have been interpreted with the nodal-plane model. Our model has also been used to analyze proton-transfer processes in thermochromic crystalline salicylidenedianilines [47]. The substituent effect in ESIPT of 1-hydroxy-2-acetonaphthone and related molecules has also supported our view [50]. For not only ESIPTs of aromatic anils [52] but also the excited-state intramolecular proton transfer of 7-azaindole dimer [54,55], the excited-state dependence of reactivity has been understood in terms of nodal-plane analysis of the wave function. Our model has also been applied to the ground-state proton transfer of salicylate anion [56]. Our explanation has also been used widely to interpret various photoreactions, in addition to proton transfer, such as the photorearrangement of o-vinyl diary1 ethers [57,58] and the photosomerization of retinal chromophore in bacteriorhodopsin [59].
In this paper, we apply our nodal-plane model to the substituent effect in the ESIPT of OHBAs. The structures of the molecules studied in this work are shown in Fig. 1. The next section briefly summarizes the mechanism of ESIPT according to our nodal-plane model. The following section describes our experiments with OHBAs and shows that the results of those experiments are consistent with our nodal-plane model. The last section summarizes our conclusions.

2. Nodal-plane model of ESIPT

OHBA can exist in two tautomeric forms: the keto form and the enol form (proton-transferred form). The relative stability of each form depends on the electronic state of the molecule, as shown in Fig. 2: in the ground state ($S_0$ state) the keto form is stable, in the first excited ($\pi$, $\pi^*$) state ($S_1^{\pi\pi^*}$ state) ESIPT takes place and yields the enol form, and in the second excited ($\pi$, $\pi^*$) state ($S_2^{\pi\pi^*}$ state) the keto form is again stable [15,17].

The equilibrium constant between the enol forms of acetylacetaldelyde [CH$_3$C(OH)=CHCHO (A form) and CH$_3$COCH=CHOH (B form)] has been determined by NMR [60]. The broken curve in Fig. 3 (double-minimum potential) shows the potential curves of the two forms. The enol forms of malonaldehyde [HC(OH)=CHCHO] can also be characterized by a double-minimum potential [61–66]. Substituting phenyl rings for the CH$_3$CCH moieties in the acetylacetaldelyde enols respectively transforms the A and B forms into the keto and enol forms of OHBA (Fig. 3). The substitution stabilizes the A form due to the resonance of the phenyl ring [67], and the keto form of OHBA becomes markedly lower in energy than the A form of acetylacetaldelyde. The B form, in contrast, is not stabilized by the
Fig. 2. Schematic representation of the $S_0$, $S_1^{(\text{H})}$, and $S_2^{(\text{H})}$ potential surfaces for OHBA. Fluor. denotes fluorescence. The broken lines indicate the nodal planes perpendicular to the molecular plane, and the dots indicate seemingly lone $\pi$ electrons.

Fig. 3. Potential curves of acetylacetaldehyde enols (broken curve) [60] and OHBA (continuous curves).

Substitution, and its energy remains essentially unchanged in transforming to the enol form of OHBA. The schematic sketch of the potential curves of OHBA thus obtained (the continuous curves in Fig. 3) is quite similar to that expected from experimental results [13,14] for the $S_0$ and $S_1^{(\text{H})}$ states of OHBA (Fig. 2): the $S_1^{(\text{H})}$ state is thought to be much more susceptible to ESIPT than the $S_0$ state. Based on Fig. 3, we suggest that the presence of the phenyl ring has a large influence on the potential curves of the $S_0$ and $S_1^{(\text{H})}$ states of OHBA.

Fig. 4 shows the nodal planes of the wave functions in several states of benzene and OHBA. As in the case of a particle in a two-dimensional rectangular potential box [68], the wave function of the $S_0$ state has no nodal plane, while the wave functions of the $S_1$ and $S_2$ states each have one nodal plane, and these nodal planes are perpendicular to each other. In the usual notation, the $S_1$ and $S_2$ states of benzene $[^1(\pi, \pi^*)]$ states are designated as $L_b$ and $L_a$, respectively [69]. Substituting CHO and OH groups for adjacent H atoms in benzene produces OHBA (Fig. 4).

In the $L_a$ state, one can write two double bonds along the nodal plane, because $\pi$ electrons are distributed over the molecule except on the nodal plane. When the two double bonds are $C_1=O_2$ and $C_3=O_4$, lone $\pi$ electrons are localized at the $C_1$ and $C_2$ atoms (Fig. 4). If ESIPT yielding the enol form takes place in the $L_a$ state of OHBA, the two lone electrons can be largely delocalized due to the formation of the $C_1=O_2$ and $C_3=O_4$ bonds. The lone electrons thus facilitate the rearrangement of the bonds to produce the enol form. The $L_a$ state of the enol form of OHBA thus becomes significantly lower in energy than the $L_a$ state of benzene.

Fig. 4. Nodal planes of the wave functions in several $[^1(\pi, \pi^*)]$ states of benzene and OHBA and the numbering system for the atoms. The broken lines indicate nodal planes perpendicular to the molecular plane, and the dots indicate seemingly lone $\pi$ electrons. Only one of the three positions of the nodal plane for the excited state of benzene is shown.
due to the delocalization, and in OHBA the $L_a$ state results in the $S_1^{\text{en}}$ state (Fig. 4). The enol form cannot take place in the $L_a$ state because $C_1 = C_1$ and $C_2 = O_2$ double bonds cannot be formed; if these double bonds were formed, the $C_1$ and $C_2$ atoms would become pentavalent. As a result, the potential energy of the $L_b$ state remains essentially unchanged.

In contrast, the wave function in the $L_b$ state of OHBA has a nodal plane perpendicular to that in the $L_a$ state (Fig. 4). ESIPT yielding the enol form cannot take place in the $L_b$ state because $C_0 = C_1$ and $C_2 = O_2$ double bonds cannot be formed: if these double bonds were formed, the $C_1$ and $C_2$ atoms would become pentavalent. As a result, the potential energy of the $L_b$ state remains essentially unchanged in transforming from benzene to OHBA, and the potential curve is not distorted much from that of the $S_0$ state of OHBA. In OHBA, the $L_b$ state thus results in the $S_2^{\text{en}}$ state (Fig. 4).

For these reasons the $S_0^{\text{en}}$ state of OHBA is thought to be far less susceptible to ESIPT than the $S_1^{\text{en}}$ state. This hypothesis is consistent with the emission properties of OHBAs [13–21, 25, 27, 28]. We are therefore led to the conclusion that the enol form is stabilized in the $S_1^{\text{en}}$ state of OHBA. In OHBA, the $L_a$ state thus results in the $S_2^{\text{en}}$ state (Fig. 4).

The enol form is preferred because of the more favorable nodal pattern in the $S_0^{\text{en}}$ state of OHBA. As a result, the potential curve is not distorted much from that of the $S_0$ state of OHBA. In OHBA, the $L_a$ state thus results in the $S_2^{\text{en}}$ state (Fig. 4).

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3. Substituent effect in ESIPT of OHBAs

In this section, we examine the absorption and fluorescence spectra of various OHBAs and discuss how...
these experimental results strongly support our nodal-plane model.

3.1. Experimental methods

Sample preparation. o-(Trifluoroacetyl)phenol (TFAP) [73,74], o-chloroacetyl)phenol (MCAP) [75–77], o-(dichloroacetyl)phenol (DCAP) [75–77], 5-methylsalicylaldehyde (MESA) [78–80] and 5-cyanoacetylaldehyde (CNSA) [78–80] were synthesized according to the methods reported previously. TFAP, DCAP and CNSA were purified by column chromatography. MCAP and MESA were recrystallized twice from petroleum ether and chloroform, respectively. THABA, MS, SA, o-hydroxyacetoephone (OHAP), o-hydroxypropophone (OHPP), salicylaldehyde (SAM), 2-hydroxy-5-methoxybenzaldehyde (MOSA), 5-chlorosalicylaldehyde (CLSA), 5-bromosalicylaldehyde (BRSA), 5-nitrosalicylaldehyde (NTSA) and 2,5-dihydroxybenzaldehyde (OHSA) were commercially obtained. OHBA, MS, SA, OHAP, OHPP and MOSA were purified by distillation under reduced pressure. SA and SAM were recrystallized twice from chloroform. CLSA and BRSA were recrystallized twice from petroleum ether. NTSAs and OHSA were recrystallized twice from a mixed solvent of petroleum ether and chloroform. Hexane and cyclohexane, which were used for spectral measurements of the o-(substituted-formyl)phenols (TFAP, MCAP, DCAP, OHBA, SA, MS, OHAP, OHPP and SAM) and 5-substituted salicylaldehydes (MESA, CNSA, MOSA, CLSA, BRSA, NTSA and OHSA), respectively, were specially prepared for luminescence and used without further purification.

Measurements. Experiments were conducted at room temperature with a 1 cm² quartz cell. The sample concentrations were about 10⁻⁵ to 10⁻⁷ M. Before measuring at room temperature, the samples were degassed by bubbling argon gas through them. The absorption spectra were measured with a Shimadzu UV-2100S spectrophotometer, while the fluorescence spectra were measured with a Shimadzu RF-5000 spectrofluorophotometer. The fluorescence spectrum signals were transferred to a microcomputer and analyzed by using the method of Mimuro et al. [81]. The fluorescence quantum yields (φ's) were determined by comparing the fluorescence spectra of the samples with that of quinine sulfate in 1 N sulfuric acid [82], after the fluorescence spectra concern had been corrected for the spectral sensitivity of the detector. Although MS and SA show dual fluorescence [83], from the fluorescence spectra we only derived the long-wavelength emission originating from proton-transferred species by using the method of Mimuro et al. [81] and determined the φ's.

3.2. Factors influencing φf

In the decay from the S¹(0) states of OHBAs, the nonradiative decay rate constant (knr) is much larger than the radiative one (kλ), as seen from the small φf of OHBA [13]. Candidates for the nonradiative decay process from the S¹(0) state include S¹(0) → S₀ internal conversion and intersystem crossing to a triplet state. The S¹(0) → S₀ decay rate constant in a solution can be analyzed in terms of the sum of the temperature-independent and -dependent decay rate constants [13,14,84]. The intersystem crossing and the radiative process in the enol tautomer are temperature-independent, while the temperature-dependent decay process, which is dominant at room temperature, has been identified as the S¹(0) → S₀ internal conversion [85]. Accordingly, it seems likely that the S¹(0) → S₀ internal conversion would be dominant in the nonradiative decay from the S¹(0) state under the present experimental conditions.

φf can be expressed with the following equation:

\[ \phi_f = k_{nr} \frac{k_{nr} + k_{r}}{k_{nr} + k_{r}} \]  

(1)

Since k_r is very small (as described above), k_{nr} + k_r is almost equal to k_{nr}. Thus, φf can be written as follows:

\[ \phi_f = \frac{k_{nr}}{k_{nr} + k_{r}} \]  

(2)

φf is proportional to the reciprocal of the S¹(0) → S₀ internal-conversion rate (k_{nr}), where k_{nr} is proportional to exp \((-\Delta E_{10}^D)\) according to the energy-gap law [86] and \(\Delta E_{10}^D\) denotes the energy difference between the zero-point vibrational levels of the S¹(0) and S₀ states; that is, the adiabatic transition energy between them. Thus,

\[ \log \phi_f \propto -\log k_{nr} \propto \Delta E_{10}^D. \]  

(3)

3.3. Results and discussion

o-(Substituted-formyl)phenols. Fig. 5a shows an example of absorption and fluorescence spectra of o-(substituted-formyl)phenols. The φf’s of the o-(substituted-formyl)phenols are given in Table 1, together with Yokawa and Tsuno’s σX constants [87–89] for the substituents bonded to the carbonyl carbon. The value of φf decreases with increasing σX. σX is a type of Hammett parameter. The Hammett equation is given by

\[ \log \sigma (\alpha) = \rho \cdot \sigma (\alpha) + \text{const.} \]  

(4)

Table 1

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Substituent</th>
<th>σX Constant</th>
<th>φf</th>
<th>ΔE_{10}^D (eV)</th>
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<tr>
<td>TFAP</td>
<td>CH3</td>
<td>+0.24</td>
<td>1.6 × 10⁻⁵</td>
<td>3.562</td>
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<td>DCAP</td>
<td>CH₂Cl</td>
<td>±0.24</td>
<td>5.2 × 10⁻⁷</td>
<td>3.586</td>
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<tr>
<td>MCAP</td>
<td>CH₃Cl</td>
<td>±1.0</td>
<td>9.7 × 10⁻⁴</td>
<td>3.689</td>
</tr>
<tr>
<td>OHBA</td>
<td>H</td>
<td>±0.4</td>
<td>8.6 × 10⁻⁴</td>
<td>3.793</td>
</tr>
<tr>
<td>OHAP</td>
<td>CH₃</td>
<td>±0.076</td>
<td>1.1 × 10⁻⁷</td>
<td>3.818</td>
</tr>
<tr>
<td>OHPP</td>
<td>C₂H₅</td>
<td>±0.089</td>
<td>8.4 × 10⁻⁷</td>
<td>3.833</td>
</tr>
<tr>
<td>MS</td>
<td>OCH₃</td>
<td>±0.28</td>
<td>1.4 × 10⁻⁵</td>
<td>4.032</td>
</tr>
<tr>
<td>SA</td>
<td>OH</td>
<td>±0.34</td>
<td>1.6 × 10⁻⁷</td>
<td>3.985</td>
</tr>
<tr>
<td>SAM</td>
<td>NH₂</td>
<td>±0.42</td>
<td>3.4 × 10⁻⁷</td>
<td>4.024</td>
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</table>
where $\sigma_n$ denotes an experimental value for a molecule with substituent $n$, $\rho$ a characteristic parameter for a given reaction, and $\sigma(n)$ a characteristic parameter for substituent $n$. Yukawa and Tsumo expressed a parameter corresponding to $\sigma$ in the Hammett equation as $\sigma = r + r\sigma_n$, where $\sigma_1$ is a normal substituent constant that does not involve any additional $\pi$-electronic interaction between a substituent and the reaction center. $\sigma_n$ is the resonance substituent constant, measuring the capability for $\pi$-delocalization of a $\pi$-electron-donating or $\pi$-electron-withdrawing substituent. As the electron-withdrawing property of a substituent bonded to the carbonyl carbon becomes stronger, $\sigma_n$ increases. $r$ is a characteristic parameter for a given reaction and measures the extent of resonance demand. The value of $\sigma_n$ does not depend on the substituted position. The reference system used in developing these parameters was the same as that used for the Hammett equation. Yukawa and Tsumo’s constants are applicable to various substituted positions of many molecules [87–89]. Since the change in the electronic structure due to the $S_0 \rightarrow S_1^{(\pi\pi)}$ excitation [$\pi(\pi^*)$ transition] mainly affects the $\pi$-bonding framework of the aromatic ring moiety, as mentioned in Section 2, the $\sigma_n$ constant is the most suitable choice as the Hammett parameter for analyzing the present experimental results. We thus plotted log $\phi_f$ against $\sigma_n$ value (Fig. 6). The plot shows a good linear relationship with a negative slope, so that as $\sigma_n$ increases, $\phi_f$ decreases.

This substituent effect can be explained by considering the nodal pattern of the wave function and the delocalization of the lone electrons in the excited states (Fig. 7). In a molecule with an electron-withdrawing substituent at the formyl group, the lone $\pi$ electron on C1 is significantly delocalized in the $S_1^{(\pi\pi)}$ state (the curved arrow in Fig. 7). Due to the delocalization of the lone electron on C1, the $S_1^{(\pi\pi)}$ state is stabilized in comparison with that of OHBA. Then, $\Delta E_{10}$ decreases (Fig. 7), and as a result, the $S_1^{(\pi\pi)} \rightarrow S_0$ internal-conversion rate constant ($k_{ic}$) increases (Eq. (3)) according to the energy-gap law [86]. Since $\phi_f$ decreases as $k_{ic}$ increases (Eqs. (1)–(3)), the $\phi_f$ value must be less than that of OHBA. The situation for a molecule with an electron-donating substituent at the formyl group is the reverse of that with an electron-withdrawing substituent. The substituent effects observed here support our nodal-plane model.

If the $S_1^{(\pi\pi)}$ potential surfaces of $\sigma$-(substituted-formyl)phenols are similar in shape to one another and only $\Delta E_{10}$ is changed by the substituent effect, the vertical $S_0 \rightarrow S_1^{(\pi\pi)}$ transition energy ($\Delta E_{10}^{(\pi\pi)}$) decreases and the photon energy at the $S_0 \rightarrow S_1^{(\pi\pi)}$ absorption maximum ($\Delta E_{abs}$) decreases with decreasing $\Delta E_{10}^{(\pi\pi)}$ (Fig. 7). Then, $\Delta E_{abs}$ is expected to decrease with increasing $\sigma_n$ according to our nodal-plane model. The values of $\Delta E_{abs}$ are listed in Table 1. As the electron-withdrawing property of the substituent bonded to the carbonyl carbon becomes stronger (that is, as $\sigma_n$ increases), $\Delta E_{abs}$ decreases. These results are also consistent with our model.

If these substituent effects based on our nodal-plane model were absent, $\phi_f$ would not show systematic dependence on the electron-donating and electron-withdrawing properties of the substituent. In fact, the $S_1 \rightarrow S_0$ fluorescence quantum yields of benzene, 1,4-bis(trifluoromethyl)benzene (CF3–Ph–CF3), p-xylene (CH3–Ph–CH3) and 1,4-dimethoxybenzene (CH3O–Ph–OCH3) in cyclohexane were estimated to be 0.07, 0.16, 0.40 and 0.21, respectively [90]. These values do not show a systematic substituent effect.

Fig. 5. Absorption (Abs.) and fluorescence (Fluor.) spectra of (a) SAM in hexane and (b) CNSA in cyclohexane. $\epsilon$ denotes the absorption coefficient. The fluorescence spectra have been corrected for the spectral sensitivity of the detector. The fluorescence spectra of SAM and CNSA were obtained by excitation at 311.0 and 333.6 nm, respectively.

Fig. 6. Plot of log $\phi_f$ against $\sigma_n$ for $\sigma$-(substituted-formyl)phenols. The plot gives a good linear fit with a slope of $-4.93 \times 10^{-4}$ and a correlation coefficient of 0.986.
in contrast to the $\phi_f$'s of OHBA, TFAP, OHAP and MS in Table 1.

5-Substituted salicylaldehydes. Fig. 5b shows an example of absorption and fluorescence spectra of 5-substituted salicylaldehydes. The $\phi_f$'s of the 5-substituted salicylaldehydes are given in Table 2, together with Yukawa and Tsuno's $\sigma_e$ constants [87–89] for the substituents at the 5-position. As with the $\omega$-(substituted-formyl)phenols, the value of $\phi_1$ decreases with increasing $\sigma_e$, and a plot of log$\phi_1$ against the $\sigma_e$ value (Fig. 8) indicates a fair linear relationship with a negative slope. As the electron-withdrawing property of the substituent at the 5-position becomes stronger, $\phi_1$ decreases.

This substituent effect can also be explained by considering the nodal pattern of the wave function and the delocalization of the lone electrons in the excited states (Fig. 9). In a molecule with an electron-withdrawing substituent at the 5-position, the lone $\pi$ electron on $C_1$ is delocalized in the $S_1$ state (the wavy arrow in Fig. 9). Due to the delocalization, $\Delta E_{abs}$ decreases, $k_{nr}$ increases and $\phi_f$ decreases (Eq. (3)), just as for $\omega$-(substituted-formyl)phenols.

The absolute value of the slope of the plot in Fig. 8 is much less than that in Fig. 6. Thus, the effect of a substituent at the 5-position on $\phi_f$ is much less than that of a substituent bonded to the carbonyl carbon. This can be attributed to the fact that the distance between the substituent and the $C_1$ atom is longer in 5-substituted salicylaldehydes than in $\omega$-(substituted-formyl)phenols.

The values of $\Delta E_{abs}$ for the 5-substituted salicylaldehydes are listed in Table 2. $\Delta E_{abs}$ increases (that is, $\Delta E_{abs}$ increases) as the electron-withdrawing property of the substituent at the 5-position becomes stronger (that is, as $\sigma_e$)

**Table 2.** Yukawa and Tsuno's $\sigma_e$ constants [87–89] for various substituents, and $\phi_f$ and $\Delta E_{abs}$ for 5-substituted salicylaldehydes in cyclohexane.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Substituent</th>
<th>$\sigma_e$ Constant</th>
<th>$\phi_f$</th>
<th>$\Delta E_{abs}$ (eV)</th>
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<td>NTSOA NO$_2$</td>
<td>+0.34</td>
<td>8.9 x 10$^{-4}$</td>
<td>3.779</td>
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</tr>
<tr>
<td>CNSSA CN</td>
<td>+0.25</td>
<td>5.3 x 10$^{-4}$</td>
<td>3.788</td>
<td></td>
</tr>
<tr>
<td>OHBA H</td>
<td>±0</td>
<td>1.0 x 10$^{-4}$</td>
<td>3.764</td>
<td></td>
</tr>
<tr>
<td>BRSA Br</td>
<td>-0.054</td>
<td>1.4 x 10$^{-3}$</td>
<td>3.626</td>
<td></td>
</tr>
<tr>
<td>CLSA Cl</td>
<td>-0.070</td>
<td>1.4 x 10$^{-3}$</td>
<td>3.629</td>
<td></td>
</tr>
<tr>
<td>MESA CH$_3$</td>
<td>-0.078</td>
<td>1.1 x 10$^{-3}$</td>
<td>3.656</td>
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<tr>
<td>MOSA OCH$_3$</td>
<td>-0.281</td>
<td>2.0 x 10$^{-3}$</td>
<td>3.426</td>
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<tr>
<td>OHSA OH</td>
<td>-0.34</td>
<td>2.2 x 10$^{-3}$</td>
<td>3.422</td>
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Fig. 9. Schematic energy-state diagram for dynamic processes in the S\textsuperscript{11} and S\textsubscript{0} states of 5-substituted salicylaldehydes. The substituent effect on the ground-state energy of the proton-transferred species is not included in this figure.

4. Conclusions

The ESIPT of OHBAs in solution has been studied by emission spectroscopy. Substituent effects on \( \phi \) can be explained by considering the nodal pattern of the wave function along with the delocalization of the \( \pi \) electrons in the excited state. The substituent effect in 5-substituted salicylaldehydes is much less than that in \( \alpha \)-(substituted-formyl)phenols.
encouragement. Last but not least, SN expresses his sincere thanks to Professor Ronald P. Steer of the University of Saskatchewan for his kind invitation to submit a paper for publication in this special issue of the Journal of Photochemistry and Photobiology, A: Chemistry, devoted to “Photon-Initiated Proton Transfer.”

References
