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Substitution Effects on the Photophysical Characteristics of the Salicylic Anion

Hem C. Joshi,[1,2] Cees Gooijer,[1] and Gert van der Zwan[1,3]

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Spectral and photophysical properties of substituted salicylic anions are investigated by steady-state and time-resolved fluorescence spectroscopy for a variety of electron donating substituents at the positions para to the hydroxyl and carboxylic groups. Next to the usual excited-state intramolecular proton transfer in aqueous solution, an excited-state intermolecular proton transfer is found to be responsible for the dual emission observed in the case of 5-aminosalicylic anions.

KEY WORDS: Salicylic anion; substitution; ESIPT; Stokes shift.

INTRODUCTION

In a previous paper [1], the salicylic anion (SA), known for its extraordinary Stokes shift resulting from a fast excited-state intramolecular proton transfer (ESIPT) reaction, was studied in a variety of solvents and solvent mixtures. The Stokes shifts were shown to be well correlated with the polarity/polarizability and hydrogen-bonding ability of the solvents involved. In general the same is true for time-resolved data. Only solvent mixtures with a water mole fraction larger than 0.8 behave exceptionally, under such conditions an additional quenching mechanism is operative, possibly because of an excited-state intermolecular proton transfer from larger-size water clusters to the salicylic anion.

The present papers deals with substituted SA. The effect of substitution on the photophysics/photochemistry of molecules undergoing excited-state *intermolecular* proton transfer reactions to the solvent has received some attention in the literature [2–4]. For example, substitution of electron withdrawing groups such as cyano or methanesulfonyl on the C-5 or C-8 position of naphthol greatly enhances the acidity of the molecule in the excited state. A few molecules that exhibit excited-state *intramolecular* proton transfer (ESIPT) have also been investigated [5–20]. Such molecules have both an acidic and a basic (proton donating and proton accepting) group, which change their signature upon excitation. This makes them particularly interesting for the study of both solvent effects and the effects of substituents.

Thus the effect of an ethoxy substituent on the ESIPT in methylsalicylate was explored by Weller [5] and later in combination with methoxy and chloro derivatives by Acuña *et al.* [6] both in the gas phase and in liquid solution. They found that, apart from the Stokes shifted band at 460 nm and a UV band at ~340 nm, these derivatives exhibit an additional band at 400 nm. The excitation spectra were observed to be identical, indicating the occurrence of an ESIPT reaction. The effect of substitution on the photophysics of salicylic acid (2-hydroxybenzoic acid) was studied in nonpolar solvents and supersonic jets by Lahmani and Zehnecker-Rentien [7], who found that for 5-methoxysalycilic acid the ESIPT reaction only takes place in the presence of a hydrogen-bond–accepting molecule such as diethylether, whereas the properties of 5-methylsalicylic acid are more or less similar to those of SA, which shows ESIPT also in the absence of such molecules.

In some recent papers the effect of substitution on the photochemical properties of salicyladimine was studied theoretically [8,9]. Here the hydrogen atom of the imino group is replaced by a variety of substituents. The

[1]Department of Analytical Chemistry and Applied Spectroscopy, Laser Centre, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands.
[2]Institute for Plasma Research, Bhat, Gandhinagar-382428 India.
[3]To whom correspondence should be addressed. E-mail: zwan@chem.vu.nl

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results indicate that the $^1\pi\pi^*$ state is not influenced by substitution, whereas the $^1n\pi^*$ gets stabilized in the SiH_3, COOH, and NO derivatives, and moreover the intramolecular hydrogen bond is weakened in the presence of NH_2, NO, CF_3, and CN substituents. The electron withdrawing groups COOH and $COOCH_3$ cause significant effects on ESIPT when they are present at specific positions in the molecule [10]. Similar effects have been reported for benzimidazole derivatives. Substitution at the 2′ position of the hydroxyphenyl group was found to have more influence on its photochemical properties than substitution at the 5′ position [11,12].

Using transient absorption and time-resolved luminescence techniques Lüdemann *et al.* [13] studied the triplet states of unsubstituted and 5-substituted derivatives of salicylic acid and methylsalicylic acid. Both compounds are considered useful matrices in MALDI (matrix assisted laser desorption ionization) mass spectrometry. The authors suggest tautomeric structures for the triplet state of these compounds and their 5-methoxy derivatives. Kasha and co-workers [14,15] reported triple fluorescence in aminosalicylates; this was attributed to molecules with normal fluorescence, molecules undergoing ESIPT, and molecules showing twisted intramolecular charge transfer (TICT). Shabestary and El-Bayoumi [16] investigated the wavelength dependence of ESIPT in *p-N,N*-dimethylaminosalicylic acid and suggested that the observed dual fluorescence comes from two different emitting states of the same conformer. For *p*-aminosalicylic acid and *p-N,N*-dimethylsalicylic acid in various solvents the occurence of ESIPT coupled charge transfer was proposed by Kim and Yoon [17,18].

In the present study we consider the effects of CH_3, CH_3O, and NH_2 groups on the 4 and 5 position of the salicylic anion, that is, on the para position with respect to the COO^-, or with respect to the OH group, respectively. In the next section we outline the experimental procedures used, and in the following section we present the results of both steady-state and time-resolved measurement performed on these compounds. The final section is devoted to a discussion and tentative explanation of the effects found.

EXPERIMENTAL

Sodium salicylate (J. T. Baker Chemicals, Deventer, Netherlands) was used as received. The other chemicals, that is, 5-methoxysalicylic acid (5-MeOSA), 5-methylsalicylic acid (5-MeSA), 5-aminosalicylic acid (5-ASA), 4-methoxysalicylic acid (4-MeOSA), 4-methylsalicylic acid (4-MeSA), and 4-aminosalicylic acid (4-ASA), were purchased from Sigma-Aldrich (U.K.) and recrystalized from ethanol. The concentration of the sample solutions used in this study was 2–5μM, unless otherwise specified.

Steady-state absorption spectra were recorded on a Cary spectrophotometer and emission and excitation spectra on a Perkin-Elmer LS-50 B fluorimeter. For excitation and emission spectra the optical density was kept below 0.1 to avoid any effect from reabsorption. Spectra were corrected for detector response and excitation source. Samples were deoxygenated completely by bubbling dry nitrogen through, because oxygen was found to quench the fluorescence significantly in organic solvents [1,21]. The effect of deoxygenation was checked by monitoring the fluorescence intensity; the process was continued until the signal maximum was reached, and no further changes occurred.

Quantum yields were determined by using quinine sulfate in 0.5 M H_2SO_4 ($\varphi_{ref} = 0.546$) as a reference and applying the following relation [22]:

$$\varphi = \varphi_{ref} \frac{A_{ref} I_s n_s^2}{A_s I_{ref} n_{ref}^2} \quad (1)$$

where I_s and I_{ref} are the integrated fluorescence intensities of the sample and reference respectively, A_s and A_{ref} are their absorbances, and n_s and n_{ref} are the indices of refraction. The precision in the quantum yield measurements is 5–10%.

Lifetimes were measured using the time-correlated, single-photon counting technique [23]. The excitation source was a Coherent Mira 900 Ti:Sapphire laser with a pulse width of ~3 ps. The laser output is frequency tripled to obtain the excitation wavelength of 295 nm. The energy is $\sim 10^{-2}$ nJ/pulse. Fluorescence was collected from the sample at a right angle through an optical system and dispersed by a spectrometer on a MCP-PMT (Hamamatsu R3809U-50) detector. Decay data were recorded with the help of a SPC-630 (Becker-Hickl) module an analyzed using Fluofit software (Picoquant). In all cases a good fit was obtained with a reduced χ^2 close to 1 and residuals distributed randomly [24]. The accuracy of the instrument was checked by recording the lifetimes of some standard compounds. Reproducibility of the lifetimes was around 50 ps. The temperature was controlled and measured by a home-built system. The precision in temperature measurements is about 1 K.

RESULTS

Substitution by the Methyl and Methoxy Groups

Upon substitution of the salycilic anion (SA) with the electron-donating methyl and methoxy groups at the 5 position, para to the hydroxyl group, the absorption as

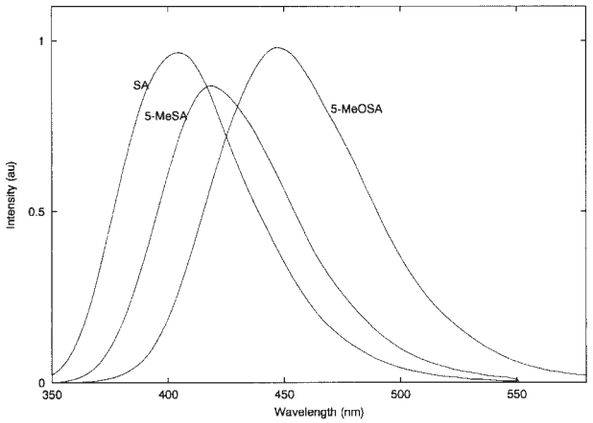

Fig. 1. Emission spectra of SA, 5-MeOSA, and 5-MeSA in water at 296 K. The excitation wavelength was in all cases 300 nm. Different slitwidths were used to record the spectra, so the intensity does not reflect the relative quantum yield. The extinction coefficients of all solutions were more or less similar.

well as the emission spectra are shifted toward longer wavelengths compared to SA. The emission spectra are shown in Fig. 1 and photophysical parameters collected in Table I. In this table we also give the Hammett constants [25] for both para- (σ_p) and meta- (σ_m) substitution. The Hammett constant is a measure of the electron-donating capability of the substituent. The excitation spectra were found to be independent of the emission wavelength and identical to the absorption spectra within experimental limits. For slightly basic solutions (pH = 9) similar spectra were obtained indicating that the compounds are more or less completely ionized in water.

The shift in the absorption and emission spectra is larger for the methoxy substituent than for the methyl substituent. The Stokes shift is larger for 5-MeOSA than for 5-MeSA. Its quantum yield is slightly higher compared to the unsubstituted SA, whereas for 5-MeSA it does not differ from that of SA.

Table I. Photophysical parameters of the salicylic anion for different derivatives substituted at the 5-position in water at 296 K.

Compound	σ_p	σ_m	λ_{abs} (nm)	λ_{em} (nm)	Δ (cm^{-1})	φ	τ (ns)
SA	0	0	296	407	9214	0.16	4.30
5-MeSA	−0.17	−0.07	305	418	8806	0.16	5.31
5-MeOSA	−0.27	0.12	319	447	9000	0.19	6.91
5-ASA	−0.66	−0.16	331	493	9927	0.03	3.42

σ_p, σ_m: Hammett constants; λ_{abs}: wavelength at the (long wavelength) absorption maximum; λ_{em}: wavelength at the emission maximum; Δ: Stokes shift; φ: quantum yield; τ: fluorescence lifetime. Measurements were done at pH 9 for the amino substituted compound, at pH 7 and 9 for the others.

Table II. Photophysical parameters of the salicylic anion for different derivatives substituted at the 4-position in water at 296 K.

Compound	λ_{abs} (nm)	ΔE (cm^{-1})	λ_{em} (nm)	Δ (cm^{-1})	φ	τ (ns)
SA	296	—	407	9214	0.16	4.30
4-MeSA	295, 239	7942	407	9214	0.11	3.04
4-MeOSA	292, 250	5635	394	8866	0.042	1.21
4-ASA	298, 265	4179	389	7738	0.014	0.62

λ_{abs}: wavelength at the absorption maxima; ΔE: energy gap between the two absorption bands; λ_{em}: wavelength at the emission maximum; Δ: Stokes shift with respect to the redmost absorption; φ: quantum yield; τ: fluorescence lifetime.

When the same groups are substituted in the 4-position, the effects are quite different, as can be seen from the photophysical parameters collected in Table II. For these compounds the emission maxima shifts are smaller (40 nm for 5-MeOSA, but 13 nm for 4-MeOSA), and in the opposite direction, that is, to the blue. A second, long wavelength absorption band appears in the absorption spectrum and at the same position in the excitation spectrum. In Fig. 2 we show the excitation and emission spectra of SA, 4-MeOSA, and 5-MeOSA for comparison. The second excitation band present around 250 nm in 4-MeOSA is quite characteristic. However, the emission spectra do not vary when changing the excitation wavelength from 292 to 250 nm; the shape and width of the emission spectra remain identical, irrespective of the wavelength of excitation. Also evident from the results given in Table II is that the position of the main absorption band barely changes, whereas, on the contrary, the second absorption band shows a large bathochromic shift

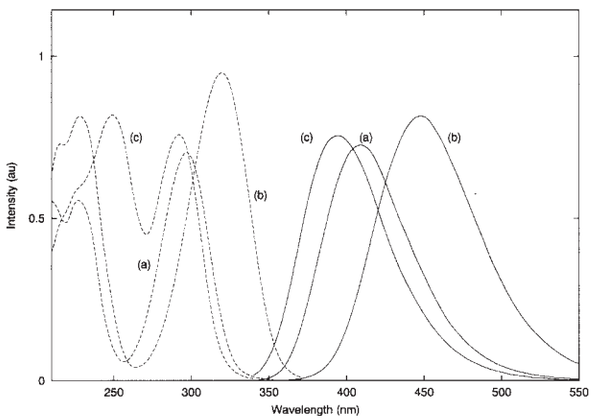

Fig. 2. Excitation (dashed) and emission (dot dashed) spectra of SA and its methoxy substituted derivatives in water. All emission spectra were obtained after excitation at 300 nm. Excitation spectra were measured at 400 nm for SA (a), 450 nm for 5-MeOSA (b), and 390 nm for 4-MeOSA (c).

Table III. Photophysical parameters of the salicylic anion for derivatives in basic methanol at 296 K.

Compound	λ_{abs} (nm)	ΔE (cm^{-1})	λ_{em} (nm)	Δ (cm^{-1})	φ	τ (ns)
SA	297	—	405	8977	0.26	6.93
5-MeOSA	321	—	444	8630	0.27	12.8
5-MeSA	307	—	416	8535	0.25	8.83
5-ASA	334	—	490	9531	0.091	9.54
4-MeOSA	292, 251	5594	389	8540	0.079	2.61
4-MeSA	298, 240	8109	403	8743	0.21	5.56
4-ASA	303, 265	4723	386	7096	0.022	1.12

λ_{abs}: wavelength at the absorption maxima; ΔE: energy gap between the two absorption bands; λ_{em}: wavelength at the emission maximum; Δ: Stokes shift with respect to the redmost absorption; φ: quantum yield; τ: fluorescence lifetime.

depending on the nature of the substituent. The energy gap between the first and second absorption band changes from 5600 cm^{-1} in 4-MeOSA to 7900 cm^{-1} in 4-MeSA. The quantum yields and lifetimes also show a decrease in the order $H > CH_3 > OCH_3$. Similar behavior is observed in basic methanol (10^{-4} *M* of KOH added) as a solvent, although the lifetimes are somewhat longer and the quantum yields slightly higher than in water (Table III). The decrease in quantum yield and reduction of the lifetime for the 4-substituted compounds correlates with the decrease in energy gap between the two absorption bands. None of these effects are observed in the 5-substituted compounds.

Substitution by the Amino Group

Substitution with the strong electron-donating amino group (both σ_p and σ_m take their lowest values for this group [Table I]) at the 5-position leads to some interesting features not observed for the methyl and methoxy substituents. In slightly acidic water (pH = 6) the absorption spectrum shows a maximum at 298 nm, with an additional broad band at ~331-nm. The 331 nm band, which again is strongly redshifted with respect to SA, is attributed to 5-ASA, whereas the 298-nm band is thought to be caused by the protonated form of the amino substituent NH_3^+SA. Evidence for this can be found by changing the pH of the solvent. At pH = 9 (data presented in Table I), only the 331-nm band is observed in the absorption spectrum, and at pH = 4 this band has vanished and only 298 nm absorption is found (Fig. 3).

In the emission spectrum two bands are found, at 408 and 494 nm, respectively, and the excitation spectra exhibit a marked difference for the two emissions (Fig. 4). The excitation spectrum associated with the 408-nm

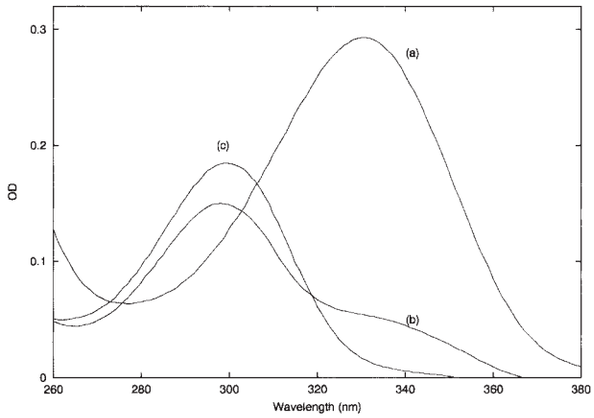

Fig. 3. Absorption spectra of 5-ASA (concentration 8×10^{-4}M) in water, at pH = 9 (a), pH = 6 (b), and pH = 4 (c).

emission shows one band, with a maximum at 298 nm; for 494-nm emission this spectrum is composed of two bands, with the longer wavelength maximum at 331 nm. The excitation spectrum for 494-nm emission is not identical to the absorption spectrum and has a higher intensity at longer wavelengths. When the pH is lowered to 4, dual emission is still observed, whereas the excitation spectrum shows only one band at 298 nm for both the 408-and 494-nm emissions (Fig. 5). The absorption spectrum then has one band at 298 nm, Figure 5. When the pH is increased to 7–9, the 408-nm band disappears and only 494-nm emission is observed. Under these conditions only the 331-nm band is present in the absorption spectrum (Fig. 3), and the same is true for the excitation spectrum (Fig. 5).

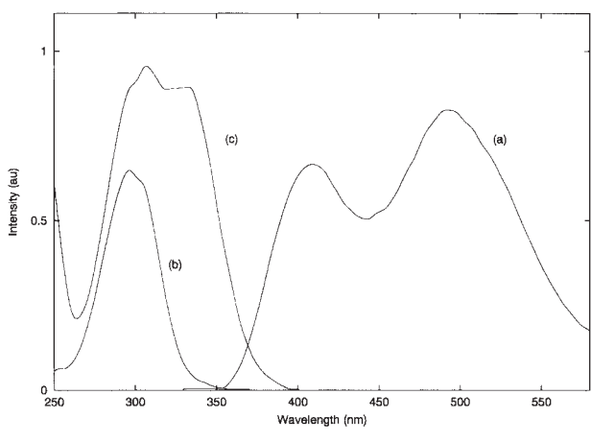

Fig. 4. Emission and excitation spectra of 5-ASA in slightly acidic water (pH = 6). (a) Emision spectrum, λ_{exc} = 300 nm, (b) excitaition spectrum for λ_{em} = 408 nm, and (c) excitation spectrum for λ_{em} = 494 nm.

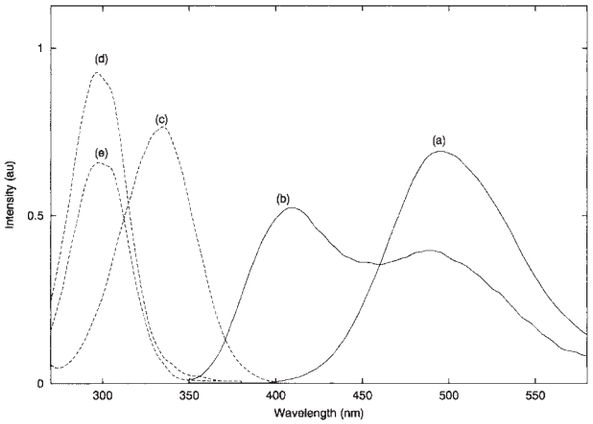

Fig. 5. Emission (solid lines) and excitation (dashed lines) spectra of 5-ASA in water under basic and acidic conditions. Emission spectra (a) at pH = 9 and (b) at pH = 4 were obtained with 300 nm excitation. For the excitation spectra the following pH values and emission wavelengths were used: (c) pH = 9, λ_{em} = 494 nm, (d) pH = 4, λ_{em} = 494 nm, and (e) pH = 4, λ_{em} = 408 nm.

Comparison of the fluorescence decay curves for 5-ASA at 408 nm and 494 nm also shows some interesting features. The decay can be fitted with a three exponential function for the 494-nm emission with two decay components of 3.4 ns and 0.55 ns, and one rising component of 0.15 ns (Fig. 6). In the 408-nm decay, no rising component is observed; it can be fitted with a two-component exponential decay function with decay times of 3.37 ns and 0.60 ns. At pH = 9, when only the 404-nm emission is present, the decay is monoexponential, with a lifetime of 3.42 ns.

Surprisingly, none of these effects is found when the amino group is substituted at the 4-position instead

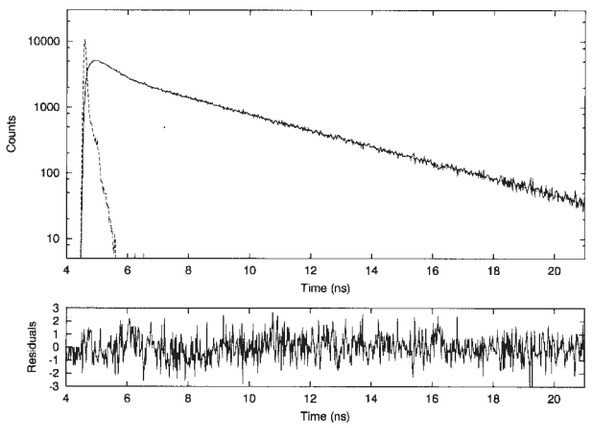

Fig. 6. Decay of 5-ASA in water for 494 nm emission. Top: decay curve and data fit (undistinguishable from data points). Also included is the instrument response (dashed). Bottom: residuals for the fit.

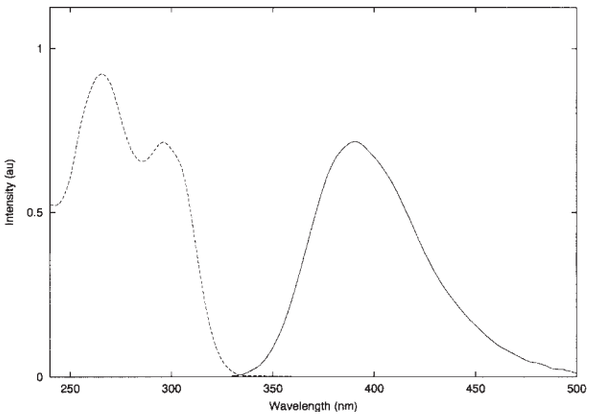

Fig. 7. Excitation (dashed) and emission spectrum (solid line) of 4-ASA in water. For the emission spectrum the excitation wavelength was 300 nm, and for the excitation spectrum the emission was monitored at 390 nm.

of the 5-position. No large Stokes-shifted emission band is observed. The emission maximum is found at 389 nm, and the absorption spectrum shows two peaks at 298 nm and 265 nm, like 4-MeOSA and 4-MeSA (Fig. 7). The gap between the first and second absorption band is smaller compared to 4-MeOSA and 4-MeSA (Table II). The excitation spectrum also shows two bands at 298 nm and 264 nm. Moreover, the emission spectra in neutral water, as well as at higher pH's, are identical and the decays fit with a monoexponential function with a lifetime of 0.62 ns.

DISCUSSION AND CONCLUSIONS

Substitution by the Methyl and Methoxy Groups

From the results it is apparent that the magnitude of the Stokes shift depends on the nature of the substituted group, Tables I and II show clearly that the Hammett constant σ_p and the Stokes shift are well correlated. The large Stokes shift in these compounds is, since Weller [5], attributed to the existence of an ESIPT reaction, so that the results demonstrate that in all the anions concerned the intramolecular hydrogen bond is still strong enough to facilitate ESIPT. For substitution at the 5-position we note that in all cases electron density at the para position (OH) is more increased than at the meta position (COO^-)—in the case of methoxy electron density is actually withdrawn from the meta position—resulting in a shift of electronic density from the COO^- group to the OH group, favoring the tautomer. The opposite is true for substitution at the 4-position.

Therefore it can be readily conceived that the magnitude of the Stokes shift behaves in an opposite way for 4-and 5-substituted compounds.

In general the lowest excited state of aromatic molecules is S_1 ($\pi\pi^*$). The appearance of a second absorption band, close to the first one, upon substitution at 4-position can presumably be attributed to the stabilization of the higher lying $n\pi^*$ state. The stabilization of an $n\pi^*$ state by substitution was, for example, predicted in the case of salicyladimine on theoretical grounds [9]. This state may also have some CT character [16] due to the presence of a substituent. Furthermore, the decrease in the gap between the two bands for groups with more electron donating character indicates a stronger interaction, and hence a lowering of this state. The effect is most pronounced for the strongly donating amino group at 4-position (Tables II and III). As was already mentioned, the second band is not present in the spectrum of the unsubstituted anion, or when the substitution is at the 5-position (Fig. 2).

It should be expected that a similar pattern of energy levels plays a role in the tautomer T formed after ESIPT. In Fig. 8 we show a possible schematic energy level diagram. Because ESIPT will only be possible in the S_1 state of N, the single emission band and identical excitation spectra for emission from the S_1' state in T can be understood. In a previous paper [1] we have shown that in aqueous solution the fluorescence of SA is quenched because of protonation of the COO^- in the excited state. Therefore we also recorded decay data in methanol (Table III), that is, under conditions in which such a quenching mechanism is not operative. From Tables I–III it is evident that, for substitution at 4-position, the lifetimes are relatively short, and consequently the quantum yields lower, indicating an increased deactivation. We also note the strong correlation of the quantum yields and lifetimes with the (Stokes) energy gap, both for substitution at the 4 and 5 positions. This enhanced deactivation can be attributed to an increased $S_1' \rightarrow T_1'$ intersystem crossing, according to the El-Sayed rule [26–28].

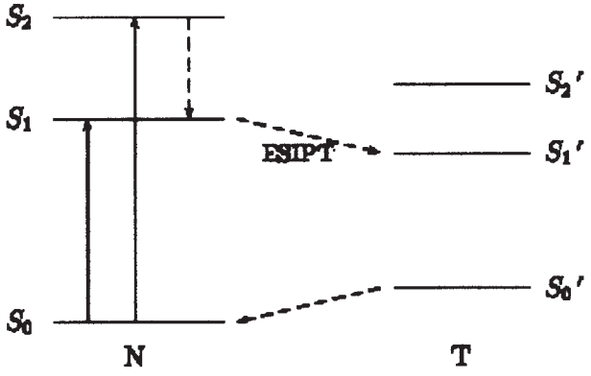

Fig. 8. Energy level diagram of the normal (N) and tautomeric (T) form of substituted salicylic anions.

Substitution by the Amino Group

To explain the dual spectral and decay results for 5-ASA we propose the scheme presented in Fig. 9. At pH = 4, 5-ASA will, in the ground state, be present as a Zwitterion (Z) with the NH_2 group protonated. Upon excitation at 298 nm the Zwitterion will undergo fast ESIPT to form T*, which emits at 408 nm. Alternatively, the excited tautomer can transfer the ammonium proton to water, resulting in the formation of an excited anion (A*), which emits at 494 nm. Although there is no direct evidence, we can expect the NH_3^+ group behaving in a way similar to OH when going from the ground to the excited state, that is, become more acidic, and loose a proton [5,29–32]. It explains the identical excitation spectra observed for both the emission bands at 408 and 494 nm. In water (pH ~6) the tail in the absorption spectrum around 331 nm can then be explained by assuming a minor amount of anions (A) present in the ground state in aqueous solution. The 331-nm band in the excitation spectrum is relatively intense compared to the tail in the absorption spectrum; this can be attributed to a higher quantum yield of A* compared to T*. At pH values significantly higher than 4, the Zwitterion completely dissociates to form the anion A in the ground state, which indeed absorbs at 331 nm and emits at 494 nm. From the absorption measurements the pK_a value for the $Z \rightleftharpoons A$ equilibrium can be estimated to be around 6.5. Unfortunately it is not possible to estimate the pK_a value in the excited S_1 state, because Z* undergoes rapid ESIPT, resulting in T*, which makes it impossible to esimate the 0–0 transitions in the emission spectrum of Z* and A*. Fluorometric titration is also not possible, because at lower pH value the COO^- group is converted to the acid form.

ESIPT reactions are extremely fast, and transition times are usually estimated below 100 fs [33–35], the observed risetime in the 500-nm emission should be attributed to the slower excited-state deprotonation of the amino group in T*. The appearance of the two decay components at 500 nm can be attributed to the fact that emissions from T* and A* partially overlap. Similarly, the biexponential decay at 400 nm is ascribed to overlapping T* and A* emissions.

For 4-ASA the situation is different. The absorption and emission spectra are similar in neutral aqueous solution, as well as at pH = 9; thus it can safely be assumed that 4-ASA is in the ground state only present as an anion.

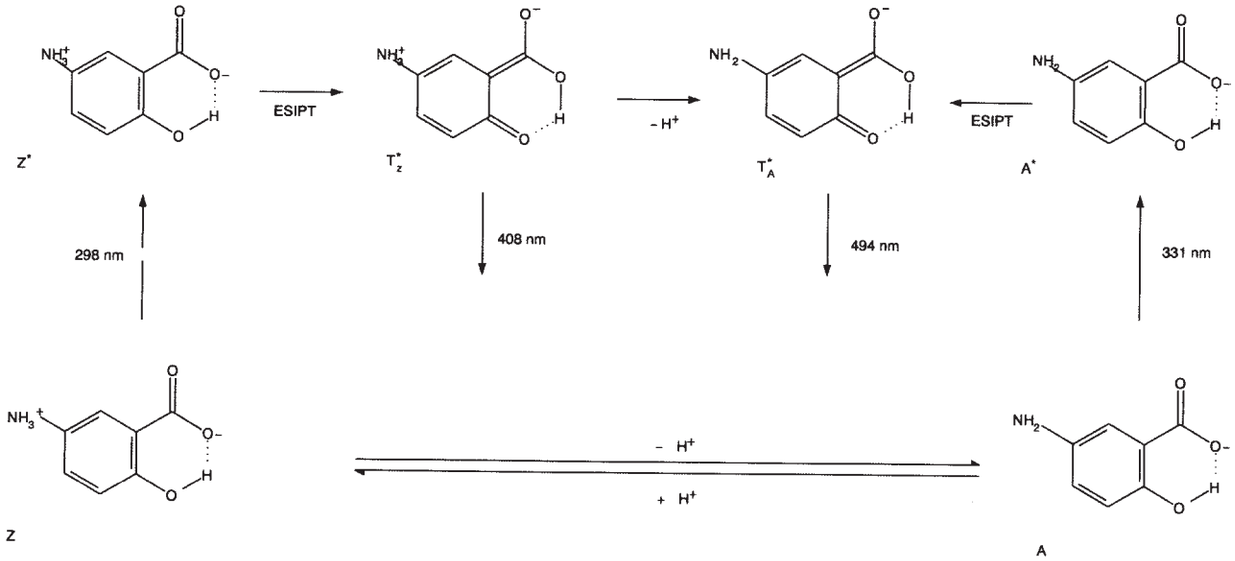

Fig. 9. Proposed reaction scheme for 5-ASA. In the ground state an equilibrium exists between the Zwitterion Z and the anion A. Upon excitation the Zwitterion undergoes tautomerization to its excited tautomer T^*_z, which can be converted to the tauomeric anion T^*_A by losing a proton. Upon excitation the anion A undergoes a rapid ESIPT reaction to its related tautomer T^*_A.

Amino substitution at the 4-position does not lead to dual fluorescence emission, unlike 5-ASA. Apparently an amino group at the 4-position is less basic, so it does not get protonated, and no Zwitterion is formed. It is likely that the character of the group para to its position is of importance here, in 4-ASA the amino group is para to the electron-withdrawing COO^- group, whereas in 5-ASA it is at the para position to the electron-donating OH group. The decreased lifetime and quantum yield compared to SA and 5-ASA might be attributed to an increased $S_1 \rightarrow T_1$ intersystem crossing, as suggested earlier.

CONCLUSIONS

In this paper the spectral and photophysical properties of substituted salicylic anions are reported. Akin to the unsubstituted salicylic anion, the substituted anions also show an emission with a large Stokes shift caused by ESIPT from the hydroxy to the carboxylic group. Substitution at the 4- and 5-positions with groups of different electron-donating capabilities shows some interesting differences. The appearance of an additional absorption band upon substitution at the 4-position is attributed to stabilization of the S_2 state of $n\pi^*$, and the simultaneous decrease in lifetime and quantum yields are explained in terms of an enhanced intersystem crossing. Dual emission in 5-ASA is attributed to excited-state intermolecular deprotonation of the NH_3^+ group. There have been very few theoretical investigations into the excited-state acidity of aromatic substituents [32], and excited-state intermolecular and intramolecular proton transfer reactions [11, 36–38]. This study shows that the variety of possible parameters should be a challenging field for a quantitative description of these phenomena.

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