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Full Paper

Excited State Intramolecular Proton Transfer in Methyl and Methoxy Substituted Salicylic Acid

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The excited state intramolecular proton transfer (ESIPT) processes in 3-methylsalicyclic acid (3-MeSA) and 3-methoxysalicyclic acid (3-MeOSA) have been investigated in cyclohexane medium by emission spectroscopic techniques. The ESIPT process was characterized in 3-MeSA from the large Stokes fluorescent band (455 nm), but it was suppressed by 3-MeOSA in cyclohexane. The ESIPT process was found to be accelerated both in 3-MeSA and 3-MeOSA in the presence of a hydrogen bond accepting agent, triethylamine (TEA). Further, theoretical calculations were carried out at the ground and excited states to complement the experimental evidences.

Keywords 3-methylsalicylic acid, 3-methoxysalicylic acid, excited state intramolecular proton transfer, fluorescence spectroscopy, AM1, DFT

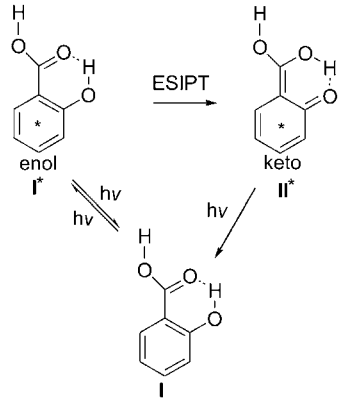
Introduction

Excited state intramolecular proton transfer (ESIPT) reaction has gained much importance in the recent years for its great scientific and technological interest, like, in the development of proton transfer lasers,[1-3] polymer-stabilizers,[4-6] Raman filters and hard-scintillation counters,[7] molecular energy storage,[8,9] fluorescent probes,[10-12] *etc*. In view of the wide practical applications of ESIPT reaction, many simple systems such as salicylic acid (SA), salicylideneaniline and their derivatives[13] were implemented to understand the photoexcitation process.

Following the pioneering work of Weller,[14] several experimental[15-18] and theoretical[19-22] studies have been devoted to study the ESIPT process in salicylic acid (SA). It was interpreted at the electronically excited state by Weller and others that a large Stokes shifted fluorescence (blue fluorescence) from the species **I** was obtained due to the formation of tautomer **II*** upon ESIPT through the vicinal hydroxyl group to the carbonyl group (Scheme 1). Another band in the UV region was also pointed, which was attributed to the fluorescence of the initially excited form **I*** in equilibrium during its lifetime with the proton-transferred form **II***.

Further work on SA derivatives such as 5-methylsalicylic acid (5-MeSA) and 5-methoxysalicylic acid (5-MeOSA) was carried out by Lahmani *et al.*,[23] and Smoluch *et al.*,[24] to see the effect of electron-donating substituents like methyl or methoxy group at the *para* position of the phenolic-OH in non-polar solvent.

Scheme 1



It was found that those of methyl substituted 5-MeSA behaved more or less similarly to SA, but the photophysical properties of the methoxy substituted 5-MeOSA were modified drastically from SA. ESIPT in 5-MeOSA is completely inhibited and only "normal" emission occurs prevailingly from its initially excited enol form. The characteristic blue fluorescence for ESIPT is suppressed and this effect was attributed to the weakening of the intramolecular O—H•••O=C bond due to the lower acidity of the phenolic-OH. However, adding some hydrogen-bond accepting molecules such as diethyl ether (DEE) or triethylamine (TEA) to the 5-MeOSA solution in cyclohexane promotes the ESIPT process again, so that both the normal band and the

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tautomeric band show up in the fluorescence emission spectrum.

Considering the pronounce effect of substitution on the photochemical behavior of SA molecules, in the present work we aimed to investigate the effects of CH_3 and OCH_3 at the 3-position (*ortho* to the phenolic-OH group) of salicylic acid in cyclohexane medium and in the presence of the hydrogen bond accepting agent, triethylamine (TEA). Molecular modeling calculations at the semi-empirical AM1 and DFT levels were carried out to complement the experimental evidences.

Experimental

Materials and measurements

The compounds 3-methylsalicylic acid (3-MeSA) and 3-methoxysalicylic acid (3-MeOSA) were obtained from Sigma-Aldrich and used directly. Spectroscopic grade cyclohexane and analytical grade triethylamine (TEA) were obtained from Merck and used directly. All the solutions taken for spectroscopic studies were prepared by dilution from the stock solution of 10^{-3} mol•L^{-1}. Absorption spectra were recorded on an Agilent-8453 diode array UV-Vis spectrophotometer. The fluorescence emission and excitation measurements were carried out in a Perkin-Elmer LS55 luminescence spectrometer at (25±1) ℃ maintained by a constant temperature circulatory bath.

Computational method

The semi-empirical calculations were carried out using MOPAC 2000 program package implemented in the Mac PC compatible CAChe version 6.1.1 (Computer Aided Chemistry).[25] First, the molecular structure was drawn in CAChe workspace and then, the initial geometry refinement was done by molecular mechanics calculation using MM3 force field. The minimized structures were then re-optimized using a semi-empirical AM1 self-consistent field (SCF) method, at the Restricted Hartree-Fock (RHF) level with convergence limit of 0.0042 kJ•mol^{-1} and RMS gradient of 0.042 kJ•mol^{-1}. The geometry at first excited singlet state was calculated using AM1 Hamiltonian by taking into account the configuration interactions CISD＝4 in MOPAC with total configuration 100. The DFT calculations of normal and tautomeric forms of 3-MeSA and 3-MeOSA have been performed both at S_0 and S_1 states by using the Gaussian 03 package.[26] The total energies of 3-MeSA and 3-MeOSA from their AM1 optimized geometry at S_0 and S_1 states were obtained by applying B3LYP functional and the configuration interaction method including only single excitations (more often indicated as CI-singles, CIS) respectively using the same 6-31G(d) basis set.

Results and discussion

The absorption spectrum of 3-MeSA and 3-MeOSA in cyclohexane at a concentration of 10^{-4} mol•L^{-1} shows maximum absorbance (λ_{max}) at 318 and 325 nm respectively, with a bathochromic shift with respect to the unsubstituted SA molecule (310 nm). The shift is similar to that reported for 5-MeSA (318 nm) and 5-MeOSA (340 nm)[23] and it is expected due to the electron-donating nature of the methyl and methoxy groups. On exciting the molecules at 300 nm (Figure 1) in cyclohexane at 10^{-4} mol•L^{-1}, the emission spectrum of 3-MeSA displayed two bands with two distinct maxima in the UV at 388 nm and in the blue at 455 nm whereas the fluorescence from 3-MeOSA exhibited a strong band at 370 nm along with a long shoulder. On comparing the fluorescence results published earlier for the 5-MeSA (380 and 450 nm)[23] and SA (*ca*. 350 and *ca*. 450 nm)[16] in non-polar solvents, it was observed that 3-MeSA behaved accordingly. The blue fluorescence peaking at 455 nm in 3-MeSA exhibited a large Stokes shift and could be associated with the tautomeric keto form, which formed in the excited state due to the transfer of proton from the hydroxy group to the carbonyl group whereas the UV band could be assigned to the direct emission from the initially excited enol form of 3-MeSA. Contrary to 3-MeSA, the fluorescence from 3-MeOSA showed a Stokes shift of 4500 cm^{-1}, which is not large enough and hence, no ESIPT process can be clearly deduced. Similar behavior was reported in the case of 5-MeOSA. Lahmani and Zehnacker[23] suggested that the relatively active group such as methoxy group in the *para* to the phenolic-OH group prevent the ESIPT process and the molecule keep similar geometry in both S_0 and S_1 states, which was also characterized under jet-cooled condition.[23] Thus, it can be inferred that similar substituents at *para* or *ortho* to the phenolic-OH group of the substituted SA molecules impact similar electronic effects and consequently, their spectroscopic behavior is alike at excited state.

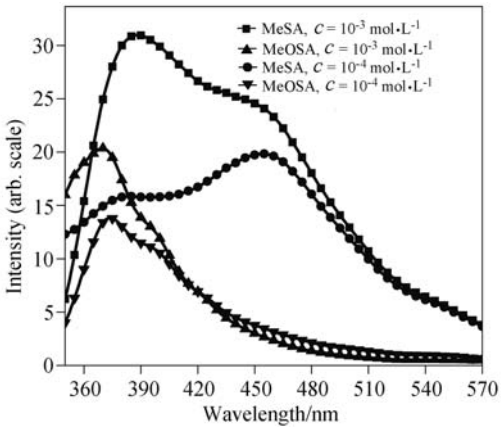
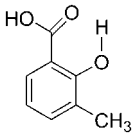
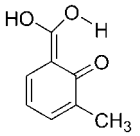
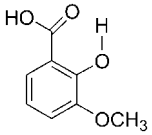
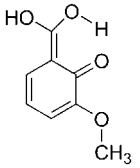


Figure 1 Emission spectra of 3-MeSA and 3-MeOSA in cyclohexane solution at different concentrations (λ_{ex}＝300 nm).

In order to get more insight into the tautomerization process at the excited state, quantum chemical calculations were carried out using semi-empirical AM1 methods. The AM1 method is claimed to describe energetics,

topographies of hydrogen bonded systems fairly accurately and also provide good estimates of geometries and heats of formation of organic molecules at the excited state.[27] The different possible tautomeric forms for 3-MeSA and 3-MeOSA were optimized both at the ground and excited state and some calculated physical parameters of 3-MeSA and 3-MeOSA are given in Table 1. The calculated ΔH_f at the S_0 state reveals that the enol form is more stable than the keto form. This is expected due to the partial rupture in the aromaticity of the benzene ring in the keto form.[28] However, at the excited state the keto form is more stable than the enol form, which possibly made the conversion of enol form into its tautomeric keto form. DFT calculations by applying B3LYP (for S_0 state) and CIS (for S_1 state) methods combined with 6-31G(d) basis set also corroborate well with the results obtained through the AM1 method (Table 1).

Table 1 Some physical parameters of 3-MeSA and 3-MeOSA calculated through semi-empirical AM1 and DFT methods.

Tautomeric forms of 3-MeSA and 3-MeOSA		AM1		AM1//B3LYP/6-31G(d) (S_0 state) AM1//CIS/6-31G(d) (S_1 state)
		ΔH_f/(kJ•mol^{-1})	E_T/eV	E_T/a.u.
	S_0	−545.66	−2096.75	−535.3623
	S_1	−189.58	−2093.07	−532.2121
	S_0	−455.23	−2095.82	−535.3278
	S_1	−259.25	−2093.79	−535.1727
	S_0	−658.71	−2416.61	−610.5593
	S_1	−323.51	−2413.14	−607.0438
	S_0	−574.17	−2415.73	−610.5256
	S_1	−378.69	−2413.71	−607.0048

The effect of concentration on the emission spectra of 3-MeSA and 3-MeOSA is shown in Figure 1. It can be observed that the shape of the fluorescence spectrum is independent of concentration but the relative intensity of the emission bands differs with concentration. The ESIPT process in 5-MeOSA was suppressed at any concentration but the intensity of UV band relatively enhanced with increase in concentration. The latter effect was also observed in the case of 3-MeSA. The influence of change in the excitation energy on the electronic properties of 3-MeSA and 3-MeOSA in cyclohexane is shown in Figure 2. The intensity of 3-MeSA emission spectrum (Figure 2a) increases successively with the increase in excitation energy without change in the peak position. Moreover, intensity of tautomeric emission increases relatively from the normal emission as excitation energy increases and becomes equal in intensity at higher λ_{exc}=330 nm. In contrast to 3-MeSA, on increase in excitation energy, the emission bands of 3-MeOSA shifted towards red (up to *ca*. 400 nm) with concomitant decrease in intensity and a long shoulder up to about 550 nm (Figure 2b). This observation suggests that change in excitation energy be unable to promote ESIPT in 3-MeOSA. Compared to results by the Smoluch *et al.*[24] for 5-MeOSA, at λ_{exc}=330 nm, the strong UV band obtained at 400 nm is characterized for the excited state structure, which is basically similar to the ground state monomeric enol form of 5-MeOSA, whereas the long shoulder for the residual ESIPT occurring in the system. Further, El-Nasr and coworkers[29] suggested through spectroscopic study on the OH stretching vibrations of jet-cooled 5-MeOSA that a large elongation of the phenolic-OH bond take place upon photoexcitation, which is responsible for residual ESIPT.

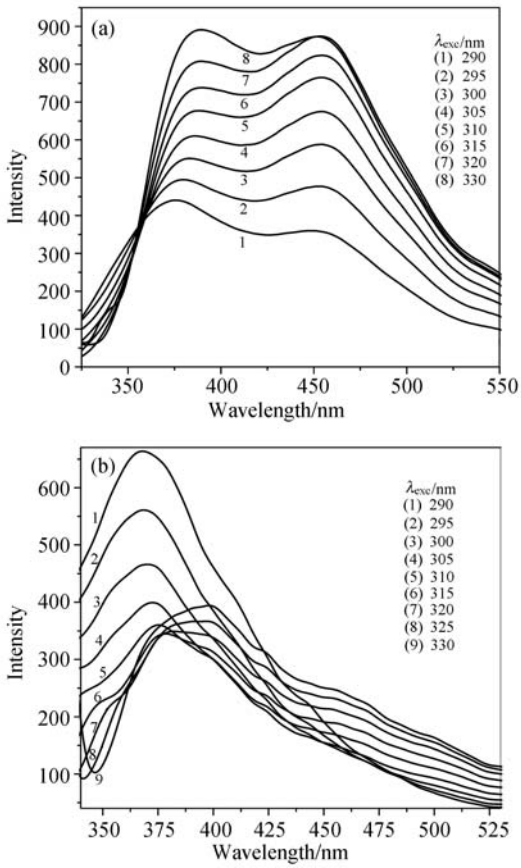


Figure 2 λ_{exc} dependent emission spectra of 3-MeSA (a) and 3-MeOSA (b) in cyclohexane solutions at [3-MeSA] = [3-MeOSA]=10^{-4} mol•L^{-1}.

Thus, the bands obtained for 3-MeOSA between 370—400 nm with the change in excitation energy could be assignable for the excited enol form of 3-MeOSA, whereas the long shoulder appeared due to residual ESIPT.

The effect of change in emission energy on the excitation spectra of 3-MeSA and 3-MeOSA is shown in Figure 3. The excitation spectrum of 3-MeSA shifted from 327 to 337 nm with the increase in emission wavelength (λ_{em}) from 380 to 450 nm (Figure 3a). The two excitation bands with different emission energy in 3-MeSA reflect the presence of two different species at the excited state: enol and keto forms of 3-MeSA, which corroborates well with the assignment made from the emission spectrum (Figure 1). Whereas, in the case of 3-MeOSA, upon increase in λ_{em} (390 to 450 nm), the intensity of the excitation spectrum of 3-MeOSA at 322 nm decreases without shift in position (Figure 3b), being possibly due to the presence of single species at the excited state.

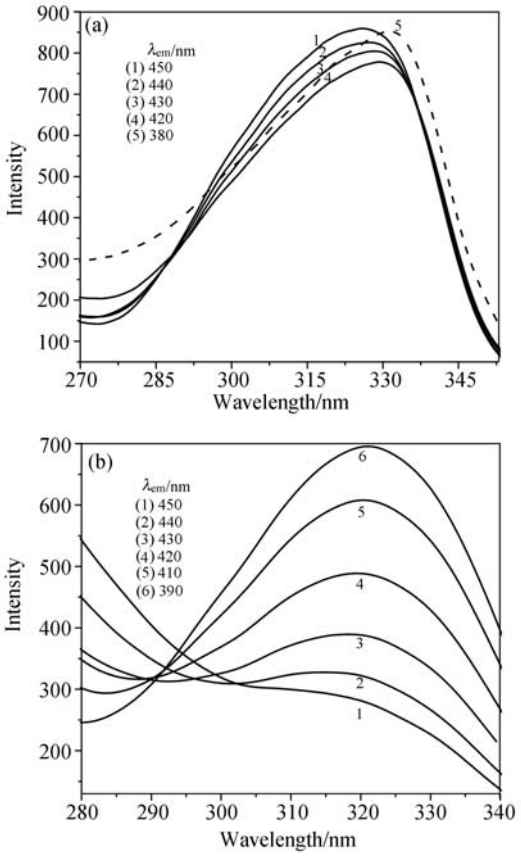


Figure 3 λ_{em} dependent excitation spectra of 3-MeSA (a) and 3-MeOSA (b) in cyclohexane solutions at [3-MeSA] = [3-MeOSA] = 10^{-4} mol•L^{-1}.

The excited-state properties of 3-MeSA and 3-MeOSA have been studied by adding a strong hydrogen bond acceptor, triethylamine (TEA). Addition of TEA (1 mol•L^{-1}) in cyclohexane solutions (10^{-4} mol•L^{-1}) of 3-MeSA and 3-MeOSA resulted in drastic changes in their fluorescence properties (Figure 4).

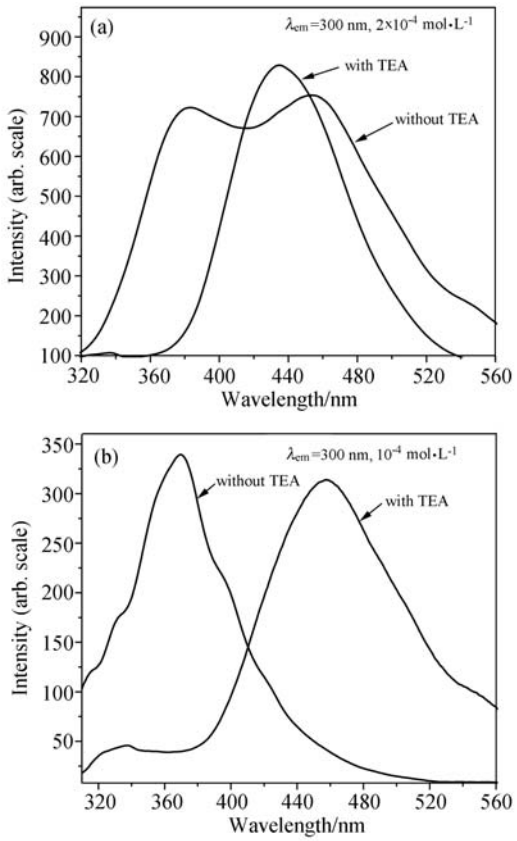


Figure 4 Emission spectra of 3-MeSA (a) and 3-MeOSA (b) in cyclohexane without and with TEA (1 mol•L^{-1}).

In both cases, the UV band is completely suppressed, leaving only the blue fluorescence. This behavior can be explained in terms of a specific complexation of 3-MeSA and 3-MeOSA with TEA involving a hydrogen bond linking between the carboxylic OH group and the nitrogen of TEA without breaking the intramolecular hydrogen bond (Figure 5). This complexation process is expected to accelerate the tautomerization process at the excited state by increasing the electron density on the C=O group and strengthening the intramolecular hydrogen bond. Again, upon complexation, no normal emission was observed, indicating that TEA promotes the ESIPT process and at the excited state the equilibrium is shifted in the forward direction from excited enol to keto form. These results are consistent well with the earlier reports on the ESIPT process of SA molecules in the presence of hydrogen bond accepting molecules.[16,23,24] Further, molecular modeling calculations were performed to complement our interpretations. The structures of 3-MeSA and 3-MeOSA, and their complexes with TEA were optimized by a semi-empirical method using RM1 Hamiltonian.[30] Some selected bond lengths (Å) and atomic charges obtained from the optimized 3-MeSA and 3-MeOSA, and their complexes with TEA are shown in Figure 5. Figure 5 clearly inferred that there be a charge transfer within the

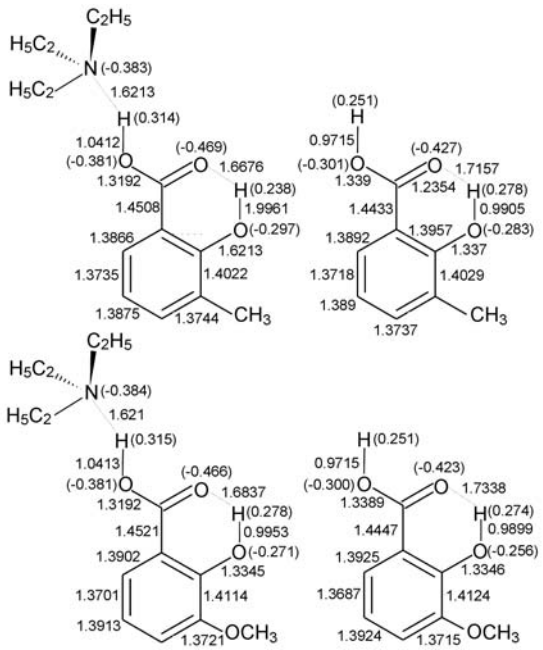


Figure 5 Some selected bond lengths (Å) and atomic charges obtained from the semi-empirical RM1 optimized 3-MeSA and 3-MeOSA, and their complexes with TEA.

intermolecular hydrogen bond from the electron-rich TEA to the carboxylic group, which in turn results in a strengthening of the intramolecular hydrogen bond. The charge transfer from TEA can also be visualized from the 2D-contour plot of total charge density (Figure 6).

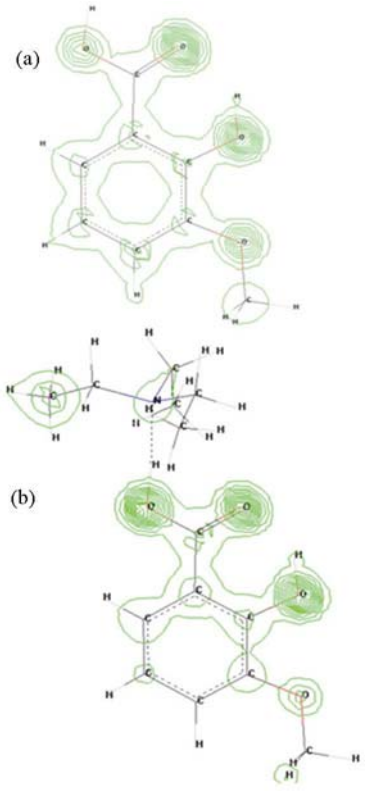


Figure 6 2D-contour plot of total charge density obtained from the semi-empirically optimized 3-MeSA (a) and 3-MeOSA (b) by applying RM1 Hamiltonian.

Conclusion

The excited state properties of 3-MeSA and 3-MeOSA are more or less similar to their respective substituted SA molecules at 5-position. 3-MeSA exhibited ESIPT whereas 3-MeOSA inhibited in cyclohexane solution. Addition of a hydrogen bond-accepting agent (TEA) suppressed the "normal" fluorescence and emission only in blue region for 3-MeSA as well as 3-MeOSA. Thus, addition of TEA accelerated the ESIPT process. The theoretical results corroborate well with the experimental evidences.

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