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Effects of Charge Transfer on the ESIPT Process in Methyl 5-R-Salicylates

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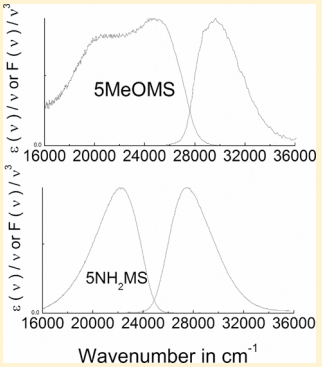
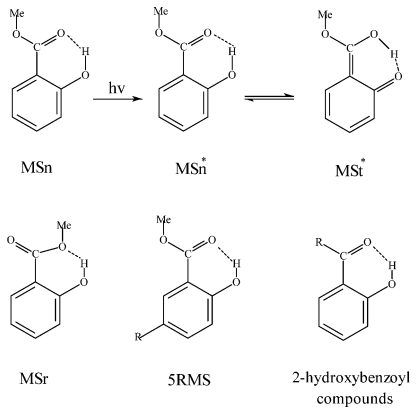
ABSTRACT: The fluorescent behavior of the methyl-5-R-salicylates is analyzed in media of negligible acidity and basicity so that the methyl-5-R-salicylates may undergo solvent dipolarity changes or not in a controlled manner based on the following guidelines: (i) The molecular forms of these methyl-5-R-salicylates possessing an intramolecular hydrogen bond (IMHB) between their hydroxyl group and ether type oxygen (rotated tautomer) undergo no excited-state intramolecular proton transfer (ESIPT) in their first excited electronic state; (ii) on the other hand, the molecular species with an IMHB between its hydroxyl group and carbonyl oxygen (normal tautomer) exhibits both ESIPT and normal emission when charge transfer (CT) from the R-substituent to the phenol group is slight to moderate, but only normal emission is monitored when CT is strong. The special insensitivity of the first UV absorption band for the normal tautomer of methylsalicylate (MS, with R = H) to the polarity of the solvent is not echoed by the normal forms of methyl-5-R-salicylates containing substituents R with a substantial effect of CT in the IMHB of the compound. These solvatochromic features of MS are shared by the emissions of its derivatives. The photophysical evidence found for the methyl-5-R-salicylates confirms the photophysical model recently reported (*Phys. Chem. Chem. Phys.* **2012**, *14*, 8903−8909), which assigns three fluorescent emissions to the methyl-5-R-salicylates: two of them coming from the IMHB normal tautomer, which undergoes ESIPT, and another from the IMHB rotated tautomer, which cannot undergo ESIPT.



INTRODUCTION

The double fluorescence of methyl salicylate (MS) in methyl cyclohexane was originally explained in 1959 by Weller[1] as follows: the fluorescence emission band for the compound (MS_n) centered at ca. 330 nm in the UV region is due to the Franck−Condon (FC) excited-state form (MS_n* in Scheme 1), whereas that located at ∼450 nm in the blue region of the spectrum is due to the proton-transfer tautomer MS_t* in Scheme 1. MS_t* results from proton transfer between the hydroxyl and carbonyl groups of MS_n*, which are linked by an intramolecular hydrogen bond (IMHB). MS_n* and MS_t* share a common double-minimum potential energy curve for the first excited π,π* singlet state of the compound.[2,3]

Scheme 1. Schematic Representation of the MS Molecular Structures



In 1980, Ford et al.[4] and Acuña et al.[5] modified the original explanation by assigning the UV emission of the compound to a rotated structure of MS (MS_r in Scheme 1). Although MS_r possesses an IMHB, it exhibits no proton phototransfer. Three years later, Heimbrook et al.[6] and Toribio et al.[7] confirmed the presence of this rotated form by free-jet and IR spectroscopy, respectively.

Recently, when MS was dissolved in 2-methylbutane (2MB) at 293 to 113 K, 1-chlorobutane (ClB) at 343 to 113 K, methylcyclohexane (Mcy) at 343 to 293 K, and squalane (SQ) at 293 to 193 K, it was found[8] to exhibit three different emissions, namely, one is due to excitation of MS_r and the other two are due to excitation of MS_n. The electronic excitation of MS_n leads to such a flat potential surface that it allows the structure to emit largely to the typical repulsion curve for the transferred form, MS_t* (hence structureless fluorescence to be emitted); also, however, this potential surface produces a weak emission at the minimum for the structure in the ground electronic state, MS_n (that shows vibronic structure) (Scheme 2).

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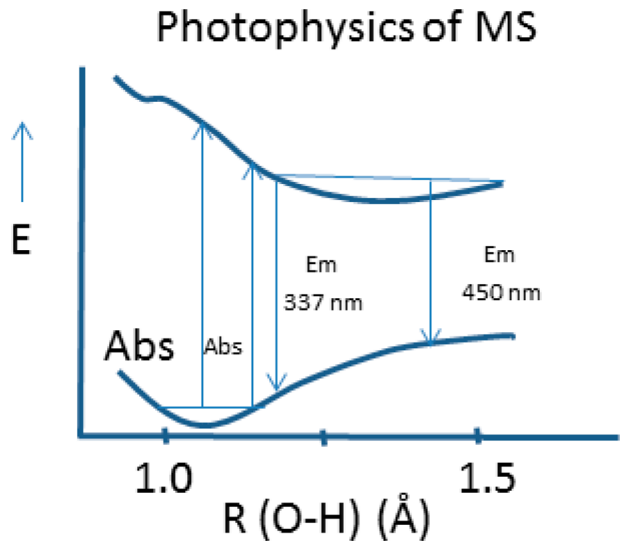
Scheme 2. Photophysical Model for the Intramolecular Hydrogen-Bonded Species of Methyl Salicylate (MS_n), Which on Photoexcitation Generates the Excited Normal Tautomer (MS_n*) That Emits at 337 nm and Its ESIPT Tautomer (MS_t*) That Emits at 450 nm[a]



[a]Third fluorescence was measured, which is not plotted in this Scheme, coming from the MS rotated tautomer (MS_r*).

To understand the process by which, according to Weller, the structure MS_n exhibits a double emission upon electronic excitation by effect of an acid−base change in the compound triggering proton phototransfer, it seems appropriate to examine its acid−base properties by introducing suitable substituents at positions altering the acidity of the phenol group mainly and assessing the resulting photophysical differences in the ensuing derivatives at position 5 of methyl salicylate. (See Scheme 1.) Especially prominent among the results obtained by following this research line are those reported by Weller et al.[3] in 1965. These authors conducted pioneering photophysical research into methyl 5-ethoxysalicylate dissolved in ClB at (20 ± 2) °C and found it to exhibit a fluorescence emission band at ca. 395 nm in addition to a shoulder in the region of 500 nm. They assigned the band to the normal structure of the compound and the shoulder to proton phototransfer from it. This evidence was clearly in support of their original proposal; in fact, the reduced acidity of the phenol group arising from the presence of an ethoxy group at a resonant position considerably inhibited proton phototransfer as a result.

In 1985, Acuña et al.[9] studied the photophysics of two new 5-derivatives of MS (viz., methyl 5-chlorosalicylate and methyl 5-methoxysalicylate) in the gas phase and in cyclohexane at (20 ± 2) °C and concluded that (a) methyl 5-chlorosalicylate in both the gas phase and cyclohexane exhibits an emission maximum at ca. 460 nm with a well-defined shoulder at 365 nm that is not detected in methyl 4-chlorosalicylate and (b) methyl 5-metoxysalicylate exhibits a maximum at ca. 395 nm and a shoulder at 490 nm, which is also absent from the emission of methyl 4-methoxysalicylate. This evidence strongly supports Weller's original assumption that the viability of the ESIPT mechanism in these compounds is governed largely by changes in their acid−base properties.

On the basis of the foregoing, proton phototransfer in these compounds should be highly sensitive to the presence of specific substituents in resonance with the hydroxyl group. In this work, we focused on methyl salicylates bearing one of the following groups at position 5: Me, F, Cl, Br, MeO, and NH_2. The compounds were studied in nonacidic, nonbasic media in order to not disturb their ability to form an IMHB and allow substantial changes in their photophysical properties to occur as a result. This is why we have not referred to evidence obtained from salicylic acids (see, for example, refs 10−15) in this Introduction; under the conditions used in this work, the acids would certainly form dimers, and such dimers are known to inhibit proton phototransfer, which occurs highly efficiently in the monomers.[15]

In this work, we examined the absorption, emission, and emission excitation of methyl 5-R-salicylates with R = Me, F, Cl, Br, MeO, and NH_2 in an inert solvent (2MB) at decreasing temperatures from 293 to 113 K and also in one with strongly temperature-dependent dipolarity[16] (ClB) over the same temperature range. The perturbations introduced by the substituents were examined in terms of their intrinsic effects, as assessed via several parameters proposed by Taft et al.,[17,18] namely, σ_R (resonance effects), σ_F (inductive field effects), and σ_α (polarizability effects). (See Table 1.)

Table 1. Substituent Parameters by Taft and Topsom[17]

substituent	σ_α	σ_F	σ_R
NH_2	−0.16	0.14	−0.52
OCH_3	−0.17	0.25	−0.42
F	0.13	0.10	−0.22
Cl	−0.43	0.45	−0.17
Br	−0.59	0.45	−0.15
Me	−0.35	0.00	−0.08
H	0.00	0.00	0.00

A substantial portion of this work involved examining the performance of the recently reported model (Scheme 2) assuming double fluorescence from the same excited electronic state[8] in the event of charge transfer from substituents at position 5 on the ring holding the IMHB in methyl salicylates.

EXPERIMENTAL SECTION

2MB in Uvasol grade (moisture content ≤0.005%) was obtained from Merck. ClB in Chromasolv grade (moisture content ≤0.001%) and 99.8% purity was supplied by Aldrich. Methyl salicylates were all supplied by Aldrich: methyl 5-fluorosalicylate (5FMS), methyl 5-chlorosalicylate (5ClMS), and methyl 5-aminosalicylate (5AmMS) in 97% purity and methyl 5-methylsalicylate (5MeMS), methyl 5-bromosalicylate (5BrMS), and methyl 5-methoxysalicylate (5MeOMS) in 96, 95, and 98% purity, respectively. All were checked to contain no impurities potentially interfering with their absorption, emission, and excitation spectra.

Methyl salicylates solutions in 2MB and ClB were prepared in such a way as not to exceed an optical density of 0.1 at the excitation wavelength (i.e., at concentrations well below 10^{-4} M). Sample temperatures ranged from 113 to 293 K and were adjusted with an Oxford DN11704 cryostat equipped with an ITC4 controller for interfacing to the spectrophotometers. The cryostat was purged with dried nitrogen 99.99% pure. All absorption, emission, and excitation spectra were recorded at a variable temperature using Suprasil cells of 1 cm light path fixed

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to the cryostat. UV−vis spectra were recorded on a Cary-5 spectrophotometer.

Corrected excitation spectra were directly recorded on an AB2 spectrofluorimeter. A small fraction of the light intensity used for excitation was switched to a Hamamatsu S1336-8BQ photodiode by means of a beam splitter. Plotting the photodiode sensitivity as a function of wavelength allowed us to characterize changes in incident light intensity at each wavelength. The ratio of emission intensity at the monitored wavelength to the corresponding excitation wavelength was used to construct absolute excitation spectra.

RESULTS AND DISCUSSION

Let us begin by examining the photophysical behavior of the methyl salicylates in such a highly inert solvent as 2MB and a special solvent such as ClB (specifically, the effect of lowering the temperature from 293 to 113 K). We will then examine their emission spectra in 2MB and ClB over the same temperature range to assess the influence of dipolarity on the photophysical behavior of the salicylates. Finally, we will examine ESIPT in these compounds in the light of the previous evidence.

Absorption Spectra. Figure 1 shows the absorption spectra for 5MeMS, 5MeOMS, and 5AmMS in 2MB and ClB

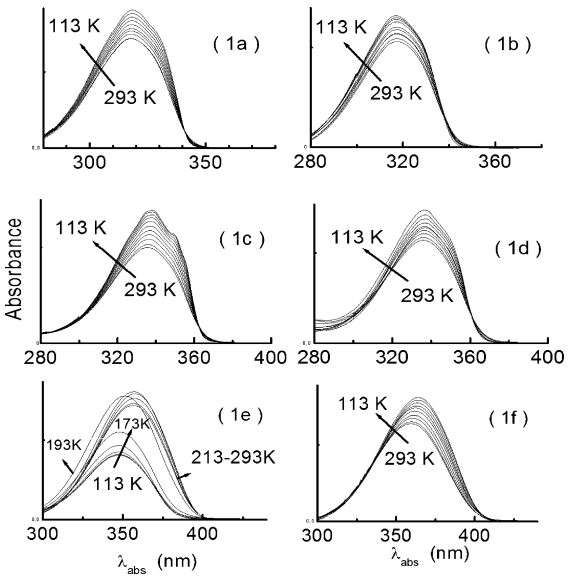

Figure 1. UV absorption spectra for 5MeMS in (a) 2-methylbutane (2MB) and (b) 1-chlorobutane (ClB) for 5MeOMS in (c) 2MB and (d) ClB and for 5AmMS in (e) 2MB and (f) ClB, recorded at temperatures between 293 and 113 K.

at 293−113 K. As can be seen from Figure 1a,b, the spectrum for 5MeMS exhibited a red shift of ca. 9 nm in its first absorption band relative to MS.[8] As in MS, the first absorption band for 5MeMS was vibrational structureless at the highest and lowest temperature studied in both solvents. As can be seen, lowering the temperature increased the spectral absorbance, largely as a result of volume contraction in the solvent, leading to a very slight increase in solute concentration.

The previous features were shared by the spectra for 5FMS, 5ClMS, and 5BrMS (not shown) except that the shifts in the maximum of the first absorption band in 2MB with respect to MS were 10.9, 11.3, and 13.4 nm, respectively. In interpreting these results, one should bear in mind that the substituents F, Cl, and Br are stronger π electron donors (σ_R, −0.15, −0.18, and −0.25, respectively) than is the Me group (σ_R, −0.08).

The aforesaid absence of vibrational structure in the spectra throughout the studied temperature range (293−113 K) suggests that the molecular structures ascribed to the two states involved in the FC absorption transition are different.

Let us now examine the spectral behavior of the salicylates containing strong electron-releasing substituents. As can be seen from Figure 1c, 5MeOMS in 2MB clearly departed from the previously described pattern; thus, the first band for the compound was vibrationally structureless above 193 K and exhibited an ill-defined peak at ca. 350 nm and a shoulder at 356 nm below that temperature level. 5MeOMS in ClB (Figure 1d) exhibited no shoulder at 356 nm, not even at 73 K. The shoulder clearly observed in 2MB was probably due to conformational isomers formed by rotation about the methoxy group; therefore, the signal at ca. 356 nm can be assigned to the less polar isomer. In a considerably more dipolar solvent such as ClB, the less polar isomer disappeared and the vibrational structure for the spectra observed at low temperatures in 2MB was therefore absent. Interpretation of the potential spectral features of the two isomers formed by twisting of the methoxy group at position 5 in 5MeOMS can be facilitated by interesting evidence of 5-methoxysalicylic acid available elsewhere.[10,13,15]

Of special note are the spectra for 5AmMS in ClB (Figure 1 f), which did not show vibrational structure throughout the studied temperature range. A comparison with the spectra in 2MB (Figure 1e) reveals that the compound exhibited an unexpected hypsochromic shift and an absorbance decrease below 193 K, followed by leveling off of the latter at 153−113 K. This spectral behavior is quite striking.

A plot of frequency at the maximum of the first absorption band for 5AmMS in 2MB as a function of temperature[19] (Figure 2) revealed that this compound occurs in monomeric form from 293 to 233 K and as clusters below 233 K (probably as a dimer that prevails below 173 K).

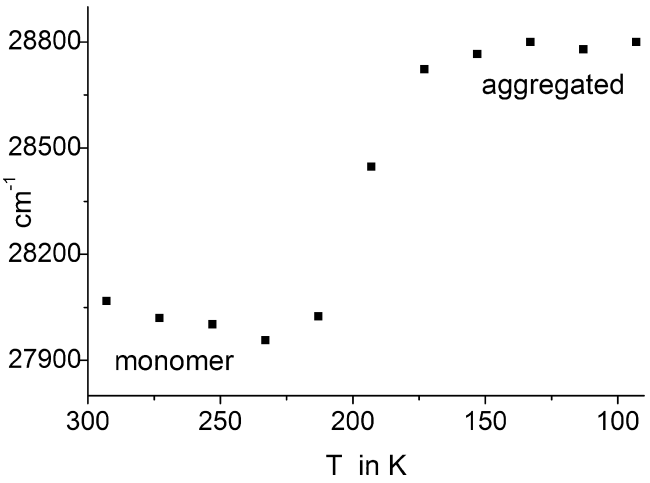

Figure 2. Thermochromic behavior of a 1 × 10^{-4} M solution of 5AmMS in 2MB.

The fact that the first band for this compound is blue-shifted with respect to the monomer suggests that it is due to (a) a dimer arranged in parallel or (b) a complex of two molecules with an open IMHB. On the basis of the excitonic model of Kasha,[20] a dimer arranged in parallel is much more likely.

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Figure 3 shows the first absorption band for the salicyl compounds and that for methyl salicylate reported elsewhere[8]

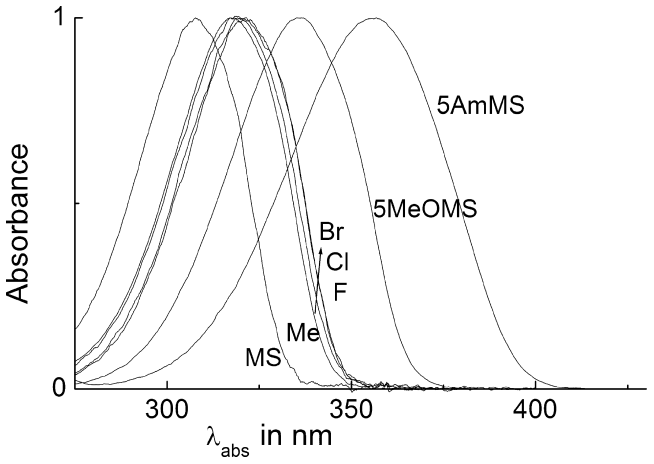

Figure 3. First band of UV absorption, normalized in their maximum, of the 5RMS studied in 2MB at 293 K.

in 2MB as normalized at the maximum. Clearly, the substituents (particularly MeO and NH_2) cause a substantial red shift in the band. The maximum energy of this band should be a function of the previously mentioned parameters of Taft and Topsom, namely:[17] σ_F (inductive field effects), σ_R (resonance effects), and σ_α (polarizability effects). In 1997, we showed[21] the first π,π^* transition in the 2-hydroxybenzoyl compounds of Scheme 1 (with R = H, Me, F, Cl, MeO, NH_2, CN, or NO_2) to fit the equation

$$\nu = (5850 \pm 1670)\sigma_R + (1990 \pm 1660)\sigma_\alpha - (3400 \pm 1320)\sigma_F + 43000 \quad (1)$$

with $n = 8$, $r = 0.944$, and SD = 840 cm^{-1}.

On the basis of eqs 2 and 3, the red shift of the band in 2MB and ClB, respectively, is governed largely by the resonance effects of the substituent at position 5 (i.e., by its π electron donor strength). Because such a position is resonant with that of the hydroxyl group, the resonance effect of the substituent must modulate the acidity of the phenol group in the compound. Therefore, the stronger the resonance effect, the lower the acidity of the hydroxyl group and the lower its proton-donor ability will be as a result

$$\nu = (7697 \pm 877)\sigma_R + (1629 \pm 693)\sigma_\alpha + (2121 \pm 853)\sigma_F + (32335 \pm 314) \quad (2)$$

with $n = 7$, $r = 0.981$, and SD = 396 cm^{-1} in 2MB and

$$\nu = (8272 \pm 962)\sigma_R + (1891 \pm 760)\sigma_\alpha + (2520 \pm 936)\sigma_F + (32413 \pm 344) \quad (3)$$

with $n = 7$, $r = 0.980$, and SD = 434 cm^{-1} in ClB.

To accurately examine the results of eqs 2 and 3, one should bear in mind that the parameters of Taft and Thompson describing resonance and polarizability effects are usually negative whereas that describing inductive field effects are usually positive. Consequently, from eqs 2 and 3, it follows that the decreased energy of the electronic transitions studied results mainly from the resonance effect of the substituents at position 5 because its polarizability and inductive field effects probably cancel each other out.

The absorption spectra for the salicyl compounds in 2MB and ClB afford several conclusions, namely:

The first absorption band for the monomeric forms of all compounds except 5MeOMs is clearly vibrationally structureless and remains so as the solution temperature is lowered. This result has important photophysical implications as it indicates that the structure of energy minimum in the first excited electronic state is significantly shifted from that in the ground state; as a result, the corresponding FC transitions cause the vibronic structure to collapse and lead to a vibrationally structureless band.

The energy of this electronic transition in the 5-derivatives is strongly affected by resonance in the substituent, which thus influences the acidity of the phenol group, a major contributor to the strength of the IMHB.

Emission Spectra for Methyl Salicylates. This analysis is initially restricted to the compounds bearing moderately resonant substituents (Me, Br, Cl, and F, with $\sigma_R \geq -0.25$) and then extended to those bearing strongly resonant substituents (MeO and NH_2, with $\sigma_R < -0.25$).

Moderately Resonant Substituents. Figure 4 shows the emission spectra for 5MeMS in 2MB and ClB at 293−113 K, as

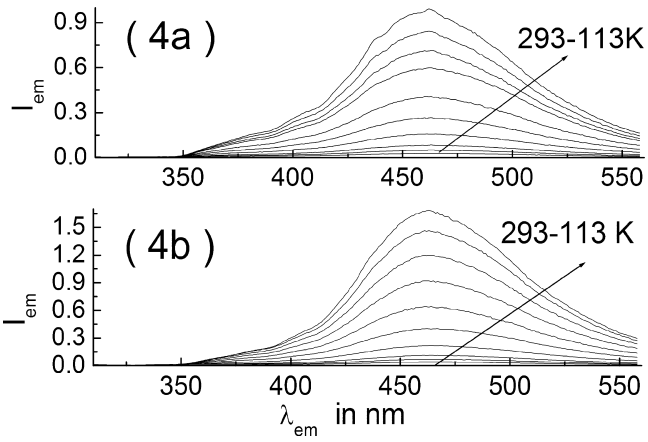

Figure 4. Fluorescence spectra on excitation at 290 nm for 5MeMS in (a) 2MB; and (b) ClB, recorded at the temperatures between 293 and 113 K.

obtained with excitation at 290 nm. Although more clearly in 2MB, the spectra in both solvents exhibited incipient structure in the form of shoulders at 360, 410, 460, and 560 nm. As previously found in MS,[8] no structured emission was observed beyond 470 nm; this further suggests that this emission band, which spans the range 340−600 nm, comprises two emissions, namely, a stronger, vibrationally structureless band due to the form resulting from proton phototransfer, $5MeMS_t^*$, on a repulsive curve in the ground state and the other due to emission of the form $5MeMS_n^*$ from the same state of the curve corresponding to the energy minimum in the ground state, as found in MS in previous work. (See Scheme 2.)

Figures 5−7 show the emission spectra for 5FMS, 5ClMS, and 5BrMS in 2MB and ClB at temperatures from 293 to 113 K as obtained with excitation at 290 nm. As can be seen, the spectra for three compounds are similar to those for MS and 5MeMS but somewhat more structured.

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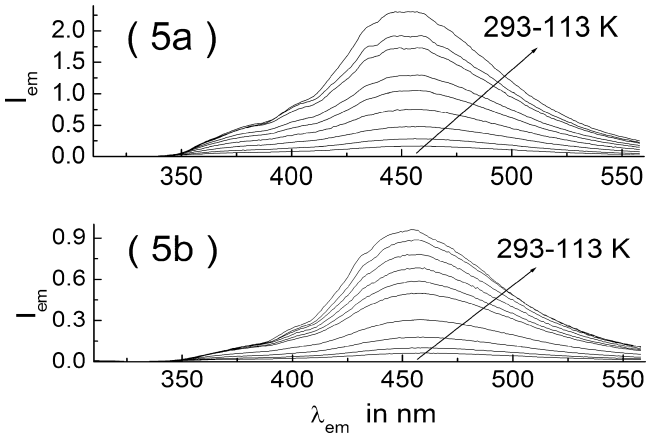

Figure 5. Fluorescence spectra on excitation at 290 nm for 5FMS in (a) 2MB and (b) ClB, recorded at the temperatures between 293 and 113 K.

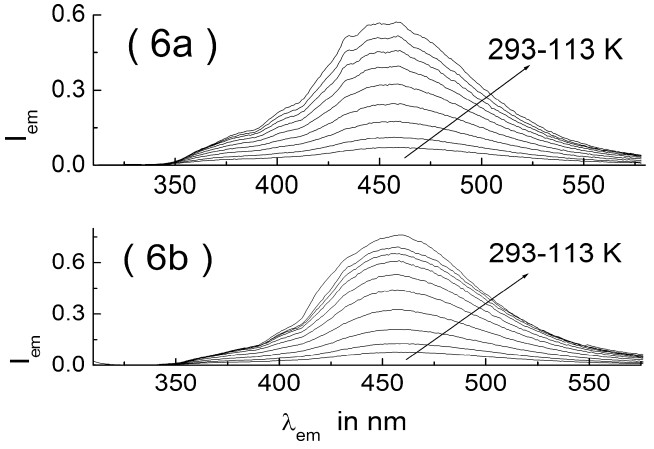

Figure 6. Fluorescence spectra on excitation at 290 nm for 5ClMS in (a) 2MB and (b) ClB recorded at the temperatures between 293 and 113 K.

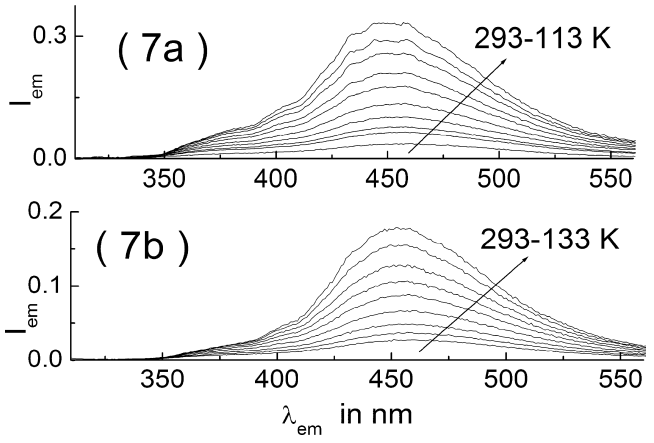

Figure 7. Fluorescence spectra on excitation at 290 nm for 5BrMS in (a) 2MB and (b) ClB recorded at the temperatures between 293 and 113 K.

The emission excitation spectra for 5MeMs, 5FMs, 5ClMS, and 5BrMS obtained by monitoring light at 530, 480, and 380 nm at 293, 213, and 133 K in 2MB, and 293, 213, and 153 K in ClB, results not shown, were consistent with the absorption spectra for these compounds.

Strongly Resonant Substituents. Figure 8 shows the emission spectra for 5MeOMS in 2MB and ClB at 293−113

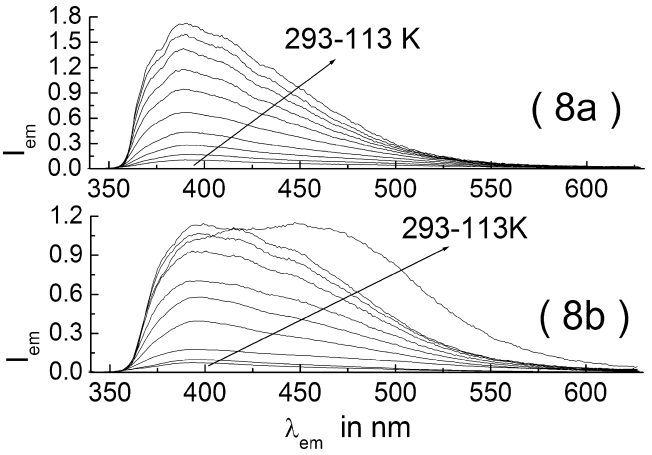

Figure 8. Fluorescence spectra on excitation at 320 nm for 5MeOMS in (a) 2MB and (b) ClB recorded at the temperatures between 293 and 113 K.

K, as obtained with excitation at 320 nm. The spectra in 2MB (Figure 8a) afford several interesting conclusions, namely:

The shoulder at 490 nm previously observed by Acuña et al.[9] in cyclohexane at 20 °C and by Lahmani and Zehnacker-Retien,[10] Mikami et al.,[12,14] and Smoluch et al.[13] under free-jet conditions, in 5MeO salicylic acid, was absent from our spectra.

Also, lowering the temperature of the 5MeOMS solution in 2MB caused the spectrum for the compound to be slightly structured (viz., to exhibit shoulders at ca. 376, 390, 410, and 433 nm, but none beyond 450 nm).

The most salient feature of the spectra in ClB is that a shoulder at ca. 450 nm became apparent at low temperatures and peaked at 113 K. This result was confirmed by spectra recorded at 93 and 77 K (Figure 9), where the new emission prevailed.

Lahmani and Zehnacker-Retien[10] previously stated the following about the shoulder in the emission spectrum for 5-methoxy derivatives in cyclohexane: "the shoulder obtained at 1700 cm^{-1} to the red of the maximum may be due to a vibrational structure" (i.e., the shoulder at 490 nm might in fact be a vibronic component of the band rather than the result of

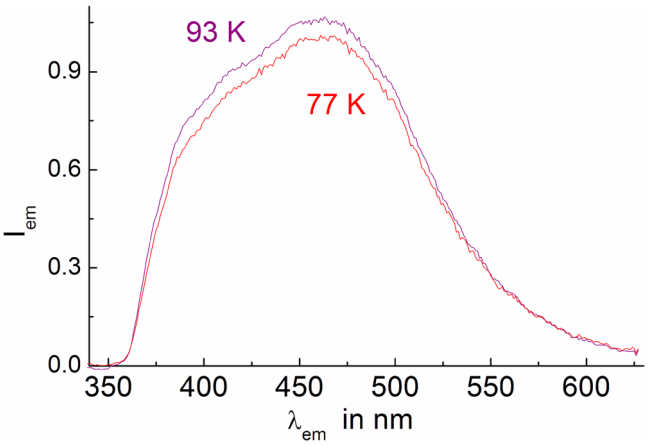

Figure 9. Fluorescence spectra on excitation at 320 nm for 5MeOMS in ClB, recorded at the temperatures 93 and 77 K.

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emission from another structure in the same electronic state). Also, they stated the following regarding the photophysics of 5-MeO salicylic acid: "The fluorescence is resonant, and its vibrational structure exhibits a mirror-image relationship with the vibronic structure observed in excitation." Subsequently, Mikami et al.[15] noted that Acuña et al.[9] had previously demonstrated a mirror-image relationship between the absorption and emission of 5MeOMS in cyclohexane at 20 °C. However, no such reference to a mirror-image relationship is seemingly made in the latter paper. It therefore seems appropriate to address the potential presence of a mirror-image relationship in 5MeOMS more rigorously.

Mirror symmetry and its implications are described in detail on pp 85 and 86 of ref 22. On the basis of them, the corrected emission spectrum obtained by dividing each emission intensity into its corresponding frequency to the cube, the absorption spectrum obtained by dividing into the frequency at each point, and the corresponding spectra as recorded on wavenumber scale should allow us to confirm whether a mirror-image relationship exists. As can clearly be seen for 5MeOMS in both 2MB and ClB in Figure 10, there is no mirror-image relationship; also, the emission spectrum for 5MeOMS at 293 K comprises two emissions: one from the normal form and the other from its transferred form.

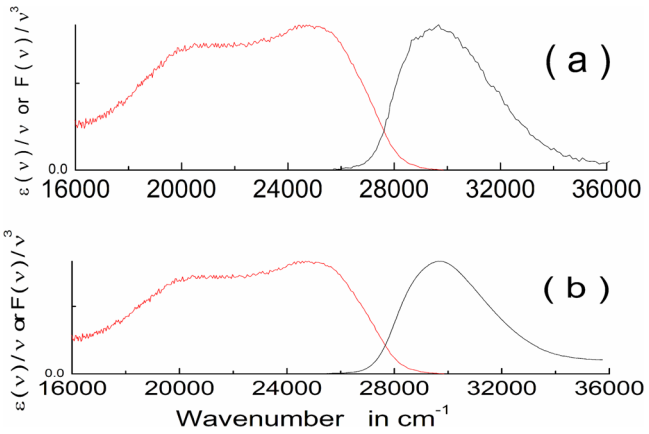

Figure 10. Mirror symmetry relation for 5MeOMS dissolved in (a) 2MB or (b) ClB at 293 K. Modified absorption band $\varepsilon(\nu)/\nu$ (black) and modified fluorescence band $F(\nu)/\nu^3$ (red).

Figure 11 shows the emission spectra for 5AmMS in 2MB and ClB at 293−113 K as obtained with excitation at 340 nm. The spectra in ClB exhibited a vibrationally structureless emission that was subject to an increasing red shift as the temperature was lowered. Consistent with previous findings from the absorption spectra, the emission of 5AmMS from 293 to 233 K was vibrationally structureless and exhibited a red shift as the temperature was lowered. In fact, from 213 to 173 K, the spectra changed in a manner suggestive of the formation of a new species (a cluster) that became the dominant form below 153 K.

The excitation spectra for 5AmMS in 2MB and ClB (results not shown) were quite consistent with its absorption spectra. Figure 12 shows the corrected emission and absorption spectra for this compound in the two solvents. Clearly, they exhibit a mirror-image relationship. Also, they confirm that 5AmMS at 293 K exhibits a single emission from its normal compounds. This evidence raises a question because neither the absorption of 5AmMS nor its emission possess vibronic structure, even

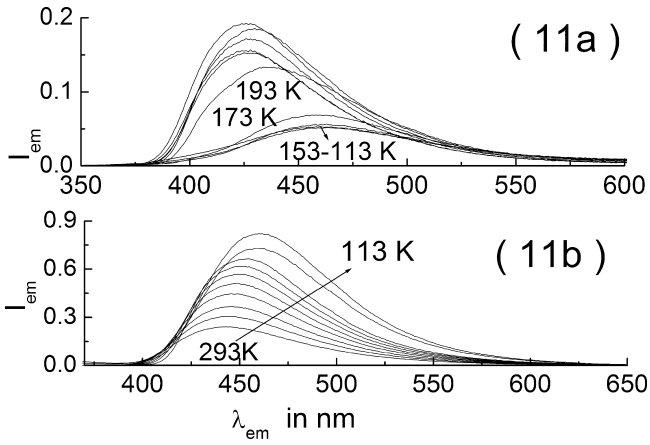

Figure 11. Fluorescence spectra on excitation at 340 nm for 5AmMS in (a) 2MB and (b) ClB recorded at the temperatures between 293 and 113 K.

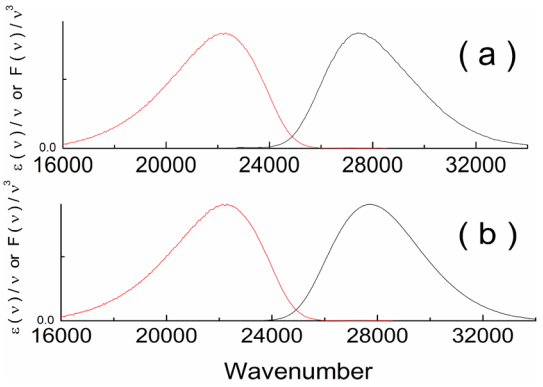

Figure 12. Mirror symmetry relation for 5AmMS dissolved in (a) 2MB or (b) ClB at 293 K. Modified absorption band $\varepsilon(\nu)/\nu$ (black) and modified fluorescence band $F(\nu)/\nu^3$ (red).

though the compound absorbs and emits from an identical molecular form.

Influence of the Substituents on the ESIPT Process. In previous work on MS,[8] we demonstrated that its photophysics is influenced by both the nature of the solvent and its temperature. As shown later, the photophysical behavior of methyl salicylates is additionally influenced by the nature of the substituent at position 5, which transfers π charge to the chelated ring forming the IMHB.

Figure 13 shows the relative intensity of the two fluorescence emissions obtained by excitation of the normal form of 5RMS, as estimated from the area under the spectral regions 350−390 nm for the normal form and 470−560 nm for the transferred form. Both areas were found to depend markedly on the nature of the solvent in both 2MB and ClB. Thus, the transferred form prevailed in 5MeMS but was much less important in the halogenated derivatives. Interestingly, both emissions were especially weak in 5BrMS, possibly as a result of its heavy atom effect.[23]

As can be seen from Figure 13b, which shows the results obtained at the three lowest temperatures studied (153−113 K) in ClB, the transferred form exhibited a substantially increased fluorescence. This was probably a consequence of gradual solidification of the solution delaying some radiationless mechanism and causing emission from the transferred form to virtually disappear as a result.

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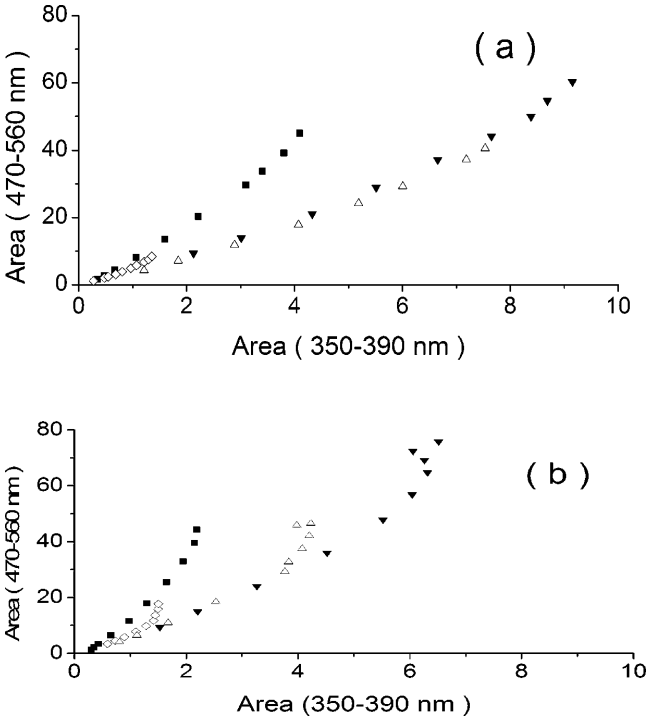

Figure 13. Fluorescence intensity of 5MeMS (■), 5FMS (▼), 5ClMS (△), and 5BrMS (◇) measured for the 470−560 nm spectral region versus that at 350−390 nm.

Clearly, the dominant role of the substituents is seemingly a result of their π electron-releasing ability; as a consequence, the substituents will transfer charge to the phenol group, and such charge will undergo delocalization and lead to an increased polarizability in the compound upon electronic excitation. If this assumption is correct, the first electronic transition in 5BrMS, 5ClMS, 5MeOMS, and 5AmMS should be sensitive to the polarizability of the medium. Because MS exhibits virtually no solvatochromism,[8] the solvatochromic behavior of its derivatives can be expected to depend little on the dipolarity of the medium. Examining the absorption maxima of the first absorption band for the target derivatives in 2MB and ClB at 293−113 K (by exception, 5AmMS was studied over the range 283−233 K in 2MB and 293−113 K in ClB for the previously described reasons) allowed us to assess the solvatochromism of 5BrMS, 5ClMS, 5FMS, 5MeOMS, and 5AmMS in terms of solvent dipolarity (SdP)[24] and polarizability (SP).[25] The ensuing equations for the different compounds were as follows:

$$\nu = -(580 \pm 138)\mathrm{SP} + (210 \pm 19)\mathrm{SdP} + (31516 \pm 89) \quad (4)$$

with $n = 20$, $r = 0.973$, and SD = 16 cm^{-1} for 5BrMS

$$\nu = -(743 \pm 131)\mathrm{SP} + (289 \pm 18)\mathrm{SdP} + (31638 \pm 85) \quad (5)$$

with $n = 20$, $r = 0.987$, and SD = 15 cm^{-1} for 5ClMS

$$\nu = -(1091 \pm 141)\mathrm{SP} + (316 \pm 20)\mathrm{SdP} + (32023 \pm 91) \quad (6)$$

with $n = 20$, $r = 0.984$, and SD = 16 cm^{-1} for 5FMS

$$\nu = -(2163 \pm 88)\mathrm{SP} + (300 \pm 12)\mathrm{SdP} + (31076 \pm 57) \quad (7)$$

with $n = 20$, $r = 0.987$, and SD = 10 cm^{-1} for 5MeOMS and

$$\nu = -(4034 \pm 670)\mathrm{SP} + (197 \pm 112)\mathrm{SdP} + (30489 \pm 409) \quad (8)$$

with $n = 14$, $r = 0.995$, and SD = 23 cm^{-1} for 5AmMS.

Equations 4−8 are arranged in increasing order of resonance effect from the substituent (−0.15, −0.17, −0.25, −0.42, and −0.52). This sequence coincides with that of the fitting coefficient of SP, which is a measure of the sensitivity of the compounds to the polarizability of the medium.

On the basis of the foregoing, the first absorption band for these salicyl compounds undergoes a marked red shift with increase in the polarizability of the medium but only a weak blue shift with increasing dipolarity.

Oddly enough, the Stokes shift between the maxima of the first absorption band for MS, 5MeMS, 5BrMS, 5ClMS, 5FMS, 5MeOMS, and 5AmMS and their emission maxima is also governed largely by the resonance effect of the substituents. Thus

$$\mathrm{DS} = (13161 \pm 2204)\sigma_R + (10998 \pm 624) \quad (9)$$

with $n = 7$, $r = 0.936$, and SD = 1060 cm^{-1} in 2MB and

$$\mathrm{DS} = (13532 \pm 2289)\sigma_R + (10921 \pm 1150) \quad (10)$$

with $n = 7$, $r = 0.907$, and SD = 1050 cm^{-1} in ClB.

Interestingly, if the substituent effects σ_F and σ_α are additionally considered, then coefficient r exceeds 0.99.

Only the normal emissions of 5MeOMS (Figure 8) and 5AmMS (Figure 11) are sensitive to the properties of the medium. In fact, the sensitivity of the solvatochromism of the corresponding emission maxima to polarizability in 2MB and polarizability and dipolarity in ClB as the temperature was lowered reflected in the following equation for 5MeOMS

$$\nu_{em} = (1223 \pm 635)\mathrm{SP} - (622 \pm 87)\mathrm{SdP} + (24829 \pm 411) \quad (11)$$

with $n = 20$, $r = 0.946$, and SD = 74 cm^{-1}.

The solvatochromic behavior reflected in eq 11 is very interesting. In fact, the emission undergoes a blue shift with increasing polarizability and a red shift with increasing dipolarity. This is consistent with the solvatochromic behavior of the first absorption band for the compound (eq 1), which is red-shifted by polarizability but blue-shifted by dipolarity. However, the coefficient of the polarizability term in eq 11 is subject to a large error (±635); in fact, if the equation is reduced to the effect of dipolarity, the solvatochromism of the band is defined by

$$\nu_{em} = -(462 \pm 43)\mathrm{SdP} + (25620 \pm 25) \quad (12)$$

with $n = 20$, $r = 0.932$, and SD = 80 cm^{-1} (i.e., the normal emission of 5MeOMS is largely governed by the dipolarity of the medium, which causes a shift red in the emission).

Similarly, the solvatochromism in the normal emission of 5AmMS can be defined as follows

$$\nu_{em} = -(1406 \pm 50)\mathrm{SdP} + (23405 \pm 37) \quad (13)$$

with $n = 14$, $r = 0.992$, and SD = 78 cm^{-1}. Therefore, the emission of 5AmMS is wholly governed by the dipolarity of the medium; in fact, the emission exhibits a marked red shift as the dipolarity is increased.

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CONCLUSIONS

Charge transfer from electron-releasing groups to the chelated ring of the IMHB in salicyl compounds plays a key role in their photophysical behavior and is thus essential with a view to understanding why excitation of the normal form results in a double emission from the same excited electronic state in some derivatives and only in the normal emission in others such as methyl 5-aminosalicylate.

It is emphasized, as originally stated by Weller, that the excited-state proton-transfer mechanism in salicyl compounds is governed by acid−base changes in the groups forming the IMHB and not to a remarkable geometrical change of the structure of the IMHB of the compound.[12,14,15]

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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