EXCITED STATE PROTON TRANSFER: A NEW FEATURE IN THE FLUORESCENCE OF METHYL 5-CHLOROSALICYLATE AND METHYL 5-METHOXYSALICYLATE†

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(Received September 26, 1984)

Summary

The fluorescence of methyl 5-methoxysalicylate and, to a lesser extent, methyl 5-chlorosalicylate departs appreciably from the usual emission of salicylic acid derivatives. The emission spectra, quantum yields and lifetimes of these compounds are compared here with those of the 4-methoxy, 3-chloro and 4-chloro derivatives which show dual emission and excitation spectra similar to those of the parent compound methyl salicylate. Moreover, the photophysics of the 3- and 4-derivatives can be understood in terms of a conformational equilibrium in the ground state and an excited state proton transfer reaction. In contrast, a new emission process with the same excitation spectrum as the proton transfer band is needed to explain the fluorescence of the 5-derivatives. It is speculated that the new fluorescence originates in those excited species which fail to undergo the proton transfer reaction despite having the appropriate intramolecular hydrogen bond in the ground state; this explanation has already been considered by Weller in the excited state equilibrium hypothesis.

1. Introduction

The fluorescence of methyl salicylate (MS) in the gas phase and in a number of solvents is characterized by two bands, the first in the blue

†Part of this work was presented at the 9th IUPAC Symposium on Photochemistry, Pau, France, 1982, dedicated to Professor A. Weller.

0047-2670/85/$3.30

region of the spectrum (450 nm) with a large Stokes shift (about 10 000 cm^{-1}) and the second in the UV (330 nm), usually with a lower intensity. This spectrum was first explained by Weller [1 - 3] who assumed that an intramolecular proton transfer reaction occurs during the lifetime of the electronically excited MS. He assigned the fluorescence with a maximum at 450 nm, which we denote here band B, to the emission of zwitterionic or quinonic species where the phenolic proton was transferred to the carbonyl group. The driving force of the transfer reaction was assumed to be the pK_a^* gradient between the carbonyl and phenol groups which in the excited state become more basic and more acid respectively. In addition, Weller assigned the weak band at 330 nm, denoted band U in this work, to "normal" electronically excited MS molecules, *i.e.* excited molecules which were in equilibrium with the zwitterionic or, in later work, quinonic [4] species.

This hypothesis has been extremely fertile and has given rise to a copious amount of research aimed at investigating the electronically induced intermolecular and intramolecular proton transfer in salicyl derivatives and in several other molecules where two functional groups with opposite pK_a^* tendencies are in close proximity [5].

According to the excited state equilibrium hypothesis, the fluorescence at 330 nm should have the same excitation spectrum as band B. It is noteworthy that this point was ignored for more than a decade. A possible explanation is that the short-wavelength fluorescence of MS is complicated by the complex solvent dependence of the emission. This is due to the simultaneous fluorescence of solvated ground state species giving rise to *inter*molecular proton transfer and, in some cases, to the presence of phenolate ion emission. When all these possibilities were taken into account it was discovered, first by Klöpffer and Naundorf [6] and afterwards by other workers [7, 8], that band B and band U do not have the same excitation spectrum. Hence the excited state equilibrium proposed to explain the MS dual fluorescence was ruled out, although it may be present in other substances.

In recent years the results of a series of spectroscopic experiments with MS and several derivatives in the gas phase and in aprotic solvents convinced us [9 - 11] that the excitation wavelength dependence of bands B and U arises from a ground state equilibrium between two rotational isomers (Fig. 1). According to this hypothesis the proton transfer band B originates from excitation of the molecular species IC which has a strong hydrogen bond between the phenol and the carbonyl groups, whereas band U is emitted by excitation of a usually small fraction (about 1%) of rotamers IIC which have an intramolecular hydrogen bond between the other oxygen atom of the ester group and the phenolic moiety. In the latter case excited state proton transfer does not take place, probably because in the S_1 state the O—alkyl group is a much weaker proton acceptor than the carbonyl group. Direct experimental evidence supporting the ground state equilibrium has been found using IR spectroscopy [12] and, to some extent, from

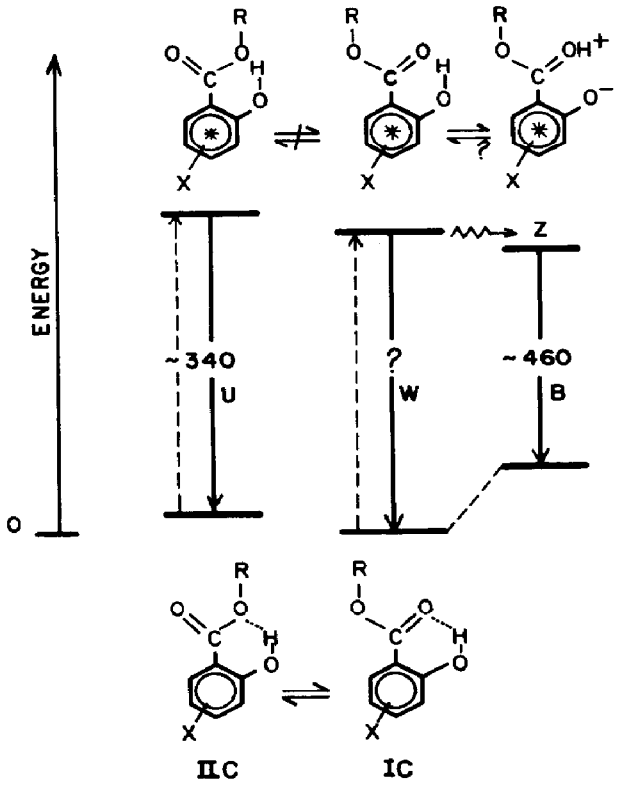

Fig. 1. The rotamer model of the photophysics of salicyl compounds in the gas phase and in solution in non-polar solvents. Proton transfer in the excited state gives species Z, which can also be described by a quinonic structure.

ultrasonic relaxation measurements [13]. Furthermore, recent high resolution excitation and emission spectra of expansion-cooled MS have also been interpreted in terms of the model summarized in Fig. 1 [14 - 17].

In contrast with what seems to be the rule in MS, the approach to an excited state equilibrium on the nanosecond time scale has been demonstrated in a few *inter*molecular proton transfer reactions, *e.g.* in 2-naphthol [18, 19]. In this case fluorescence emission from both the neutral molecule and the naphtholate ion can be observed. This is due in part to a slower proton transfer rate than in MS where the reaction is completed in less than 10 ps [20]. Hence, if a similar slowing down of the intramolecular transfer rate occurred in a salicyl derivative, the excited neutral molecules might survive long enough to emit a third fluorescence (band W in Fig. 1) in addition to the dual-band system discussed above. In this work we report several experiments indicating that a new fluorescence band is present in salicylic acid derivatives substituted in position 5. To confirm this finding the emission spectra of MS containing a chlorine atom or a methoxy group in different ring positions were recorded and compared. We provide a tentative explanation for the remarkable emission from methyl 5-methoxy-

salicylate which, like that of the 5-ethoxy derivative reported 20 years ago [4], stands out as a spectroscopic rarity in the photophysics of salicyl derivatives.

2. Experimental details

2.1. Materials

3-Chlorosalicylic acid [9] and 5-chlorosalicylic acid were obtained by the chlorination of salicylic acid in CCl_4 with *tert*-butyl hypochlorite and were separated by chromatography. 5-Chlorosalicylic acid (melting point, 172 - 173 °C (H_2O) (literature value, 171 °C [21])) was the main reaction product. Methyl 3-chlorosalicylate (3 ClMS) (melting point, 35 °C) [9] and methyl 5-chlorosalicylate (5 ClMS) (melting point, 45 - 47 °C (literature value, 47 °C [22])) were obtained from the corresponding acids by reaction with methanol (MeOH)–HCl and diazomethane respectively and were purified by crystallization from MeOH. Repeated treatments of methyl 5-chlorosalicylate with D_2O in acetone or deuterated methanol (MeOD) at 30 - 40 °C followed by vacuum evaporation of the solvents and a final crystallization from MeOD yielded the 90%-deuterated ester methyl 5-chlorosalicylate-*d* (5 ClMSD). Methyl 4-chlorosalicylate (4 ClMS) (melting point, 27 - 28 °C (literature value, 27 °C [23])), methyl 4-methoxysalicylate (4 MeOMS) (melting point, 50 °C (literature value, 51 °C [24])) and methyl 5-methoxysalicylate (5 MeOMS) [25] (boiling point, 88 °C at 0.5 Torr) were prepared from the corresponding commercial acids (Aldrich) with diazomethane, and were purified by column chromatography (silica gel, $CHCl_3$) and crystallization from MeOH or vacuum distillation. All esters gave single spots on thin-layer chromatography plates in several eluents and their IR spectra, mass spectra and proton magnetic resonance spectra were in agreement with their structures.

All the solvents used in these syntheses were free from fluorescent impurities. Cyclohexane (Merck; for fluorometry) was dried by distillation over sodium.

2.2. Methods

The spectra of the compounds studied here were recorded in the gas phase at very low pressures and in solution at low optical density (less than 0.04). This facilitated the early detection of solvent-dependent artefacts. The vapours of these substances at room temperature (20 ± 2 °C) were handled in a grease-free high-vacuum line using conventional or spherical cells as described elsewhere [10 - 12]. The emission and excitation spectra were obtained using an SLM 8000D digital fluorometer and were processed on a PDP 11/05 minicomputer. The spectra presented here are in photon units and have been corrected for instrumental factors. Solution fluorescence quantum yields were measured with reference to quinine bisulphate in 0.1 N H_2SO_4 ($\phi_F = 0.51$) [26]. The estimated error is 10% -

20%, but it can be as high as 30% for the lowest yields. The fluorescence lifetimes were determined using time-correlated single-photon counting on a spectrometer equipped with Ortec electronics and a nanosecond flash lamp (EI 199, Edinburgh Instruments). The emission was isolated using interference filters and the decay curves were analysed by iterative convolution using the PDP 11/05. The colour shift of the emission photomultiplier was experimentally measured using standard single-exponential compounds.

Absorption spectra were recorded on a Cary 219 spectrophotometer using 10 cm silica cells for the low pressure gas phase spectra.

3. Results and discussion

3.1. The fluorescence of methyl 3-chlorosalicylate and methyl 4-chlorosalicylate

The emission spectra of 3 ClMS at a pressure in the 10^{-3} Torr range measured in a cell previously evacuated to 10^{-6} Torr are shown in Fig. 2. The dual band closely resembles that of the parent compound MS [10]. For the purpose of this paper we denote the blue emission as band B and the UV emission as band U. The relative intensity of the two bands changes progressively with the excitation energy, and two excitation spectra can be determined for bands B and U (Fig. 2). The intensity maxima of the excitation bands are displaced relative to the absorption maximum (Table 1). By analogy with the parent compound MS [9] we associate the excitation spectrum at 330 nm with rotamer IC in Fig. 1, while the spectrum at 308

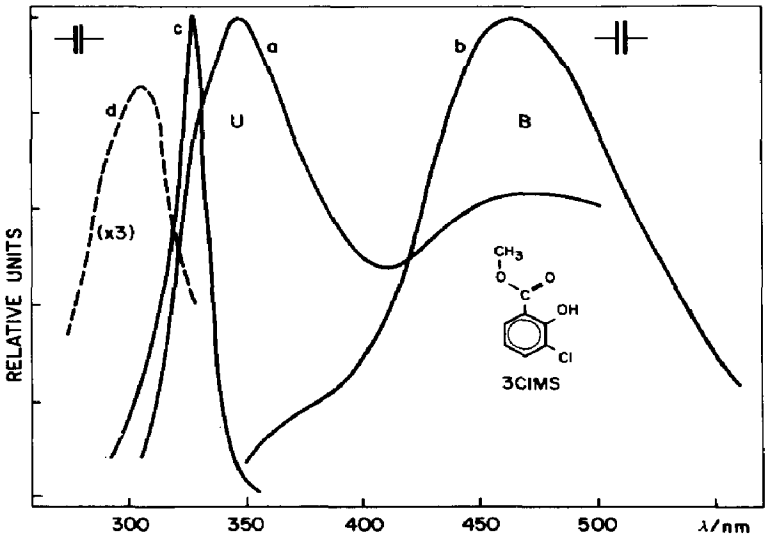

Fig. 2. Gas phase fluorescence spectra of 3 ClMS: emission spectra at λ_{ex} = 335 nm (curve a) and λ_{ex} = 300 nm (curve b); excitation spectra at λ_{em} = 480 nm (curve c) and λ_{em} = 350 nm (curve d).

TABLE 1

Gas phase spectroscopic data for the chloro and methoxy derivatives of methyl salicylate in the collision-free limit at 20 °C

Compound	λ_{max}(abs) (nm)	λ_{max}(exc) (nm)	λ_{max}(fluo) [a] (nm)
3 ClMS	311.5	308, 330	350, 465
4 ClMS	302.5	303, 318	333, 450
5 ClMS	316	315, 333	365[b], 460
4 MeOMS	297	—[c]	320, 455[c]
5 MeOMS	333	347	380, (490)
MS[d]	303.5	298, 324	330, 445

[a]The position of the blue maximum depends on the excitation wavelength.
[b]For λ_{exc} = 300 nm (see text).
[c]Poor signal-to-noise ratio.
[d]See ref. 12.

nm is assigned to species IIC. The shift in the maximum and the sharp fall-off of the 330 nm band [10] results from the fast decrease in the blue emission yield on increasing the excitation energy. This efficient non-radiative decay appears at an excess vibrational energy of 1500 cm^{-1}, which is close to what is observed in MS [10, 16].

In non-polar solvents band U is extremely weak in the fluorescence of 3 ClMS, and only band B is included in Table 2. The excitation spectrum of this band follows the absorption spectrum closely (Table 2) because thermalization of the excess excitation energy through solvent collisions

TABLE 2

Spectroscopic data of chloro and methoxy derivatives of methyl salicylate in degassed cyclohexane solution

Compound	λ_{max}(abs) (nm)	λ_{max}(exc) (nm)	λ_{max}(fluo) (nm)	ϕ_F[a]	τ_F[b] (ns)
3 ClMS	315	315	—, 475	0.045	0.85
4 ClMS	306	306	—, 445	0.055	1.0
5 ClMS	322	322	375, 460	0.08	1.47
4 MeOMS	298	293, 298	323, 460	0.007	—
5 MeOMS	338	338	395, (490)	0.11[c]	1.2[c]
5 EtOMS[d]	—	—	400, (490)	—	—
2 MeOMB[e]	—	—	352	—	—
MS[f]	308	300, 308	335, 454	0.022	0.28

[a]Quantum yield of the fluorescence under the blue band.
[b]Lifetime of the fluorescence under the blue band.
[c]Data for the most intense emission at 395 nm.
[d]See ref. 4.
[e]Methyl 2-methoxybenzoate, see ref. 2.
[f]See ref. 12.

"cools" the emitting molecules. This was confirmed by recording the gas phase excitation spectra of these compounds in the presence of increasing amounts of a buffer gas (*n*-propane) which acts as the collisional partner. A broadening of the 330 nm excitation band with a red shift of the maximum can be observed at higher buffer pressures.

The emission from 4 ClMS in the gas phase (Fig. 3) differs from that of 3 ClMS only in the position and relative intensity of the band maxima. The excitation in the long-wavelength tail of the absorption band gives rise to what is essentially a single band B spectrum. Therefore the fluorescence assigned to species IIC (band U) can be isolated by the difference between two spectra recorded at widely different excitation energies. This has been carried out and the results are shown in Fig. 3. By comparing the maximum of the difference band with that of its excitation spectrum a Stokes shift of about 3000 cm^{-1} can be estimated for the fluorescence of rotamer IIC. A red shift in the maximum of band B, which is produced by increasing the excitation energy, is clearly observed in Fig. 3, as in MS [12]. The reverse effect, *i.e.* a blue shift at higher energies, has been described recently in the MS fluorescence from a supersonic jet [16]. The very different vibrational temperatures of ground state molecules in the two experiments may be related to these contradictory observations. In cyclohexane solution only band B is clearly seen in 4 ClMS (Table 2) with a lifetime quite similar to that of 3 ClMS.

3.2. The fluorescence of methyl 5-chlorosalicylate

The gas phase emission spectra of 5 ClMS for excitation energies from the blue side (300 nm) to the red tail of the absorption band (Table 1) are shown in Fig. 4. Although the fluorescence is apparently similar to that of

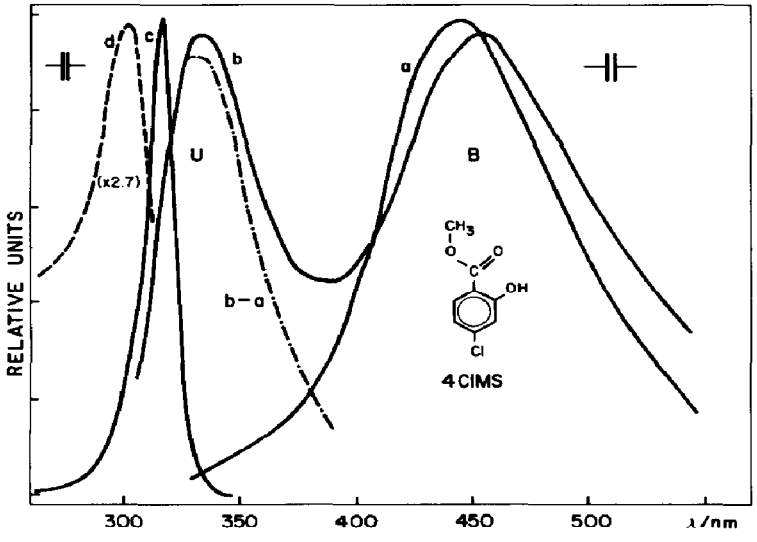

Fig. 3. Gas phase fluorescence spectra of 4 ClMS: emission at λ_{ex} = 320 nm (curve a) and λ_{ex} = 290 nm (curve b); excitation spectra at λ_{em} = 440 nm (curve c) and λ_{em} = 335 nm (curve d); — · —, emission band U which is the difference between spectra b and a.

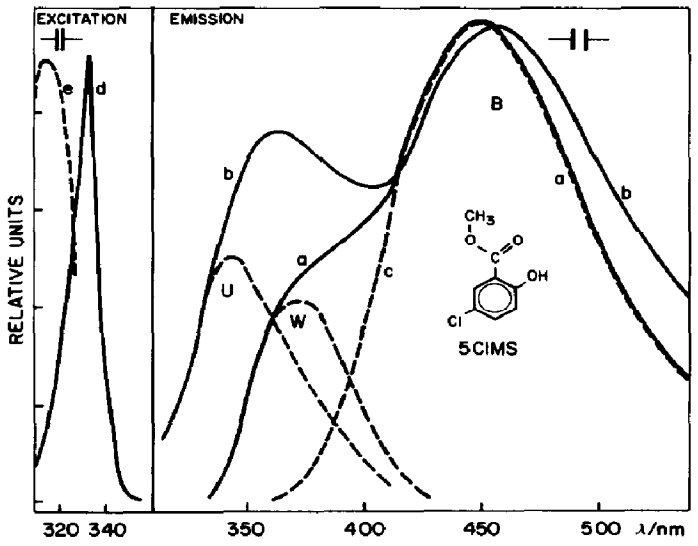

Fig. 4. Gas phase fluorescence spectra of 5 ClMS: emission at λ_{ex} = 350 nm (curve a) and λ_{ex} = 300 nm (curve b); excitation spectra at λ_{em} = 450 nm (curve d) and λ_{em} = 330 nm (curve e); band U is the difference between spectra b and a; band W is the difference between spectrum a and the emission of 4 ClMS (spectrum c).

MS, a new feature appears: the blue band B at 460 nm is always associated with a shoulder at about 365 nm, even at the longer excitation wavelength, giving enough emission to be recorded (about 350 nm). This shoulder can also be observed in the solution spectrum of Fig. 5. In these last conditions, the fluorescence does not change with the excitation wavelength, *i.e.* the shoulder shows the same excitation spectrum as the main band B. The

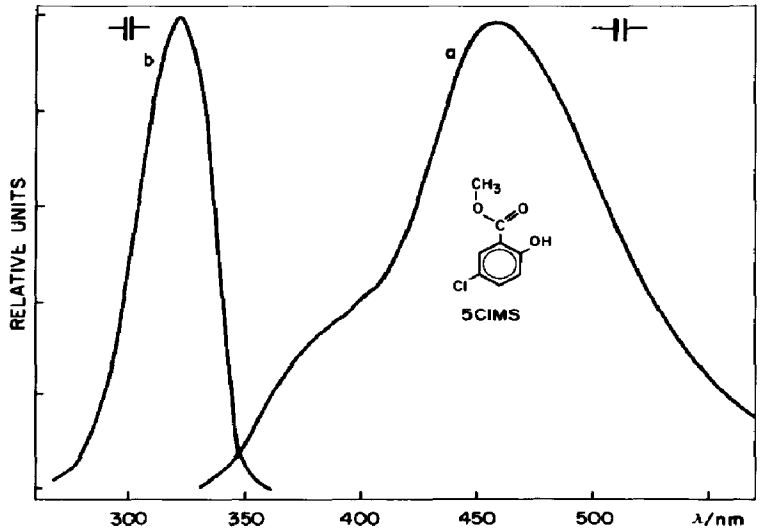

Fig. 5. Fluorescence spectra of 5 ClMS in degassed cyclohexane: curve a, emission spectra for λ_{exc} from 280 to 350 nm (all spectra overlap on the same line); curve b, excitation spectrum for λ_{em} = 500 nm (this spectrum does not depend on λ_{em} in the range 350 - 510 nm).

intensity of this weak band, here designated band W, did not increase when the cyclohexane solution was degassed, although we have shown before [12] that this procedure enhances the UV emission from salicyl compounds. In addition, gas phase experiments carried out at several temperatures from 10 to 60 °C showed only a slight increase in the relative intensity of band W. It seems very likely that band W is a new emission which is not present in either 3 ClMS or 4 ClMS. According to these results the gas phase fluorescence of 5 ClMS was decomposed into three different contributions: (i) the main band B which characterizes the proton transfer molecular species, (ii) the familiar band U from the excitation of rotamer IIC and (iii) the new band W. The following procedure was followed to estimate the shape and position of the new band in Fig. 4. It was inferred from the data presented above that it is unlikely that band B of 5 ClMS would differ greatly from the analogue emissions in 3 ClMS and 4 ClMS. Therefore band W was obtained by subtracting band B of 4 ClMS (λ_{ex} = 350 nm) from the fluorescence of 5 ClMS excited in the red tail of the absorption. In addition, band U of 5 ClMS was obtained in the same way as described before for 4 ClMS. The result of this (quite evolved) decomposition is summarized in Fig. 4. Only two maxima were recorded in the excitation spectra because bands B and W show the same one.

The experimental quantum yield of the 460 nm fluorescence of 5 ClMS in cyclohexane (Table 2) is considerably larger than that in the parent compound MS. In previous work [12] we used a simple relationship between the assumed fluorescence yield ϕ_{FZ} of the species Z in Fig. 1 and the experimental emission yield ϕ_F which can be expressed as follows.

$$\phi_F = \phi_Z \phi_{FZ} \tag{1}$$

$$\phi_{FZ} = \frac{\tau_{F(Z)}}{\tau_{R(Z)}} \tag{2}$$

where ϕ_Z is the proton transfer efficiency or, alternatively, the yield of the population of Z states by excitation of S_0(IC) molecules. According to eqn. (1) the higher ϕ_F of 5 ClMS could originate in an increased proton transfer reaction or in a more fluorescent Z species. The first possibility is unlikely because ϕ_Z already approaches unity in MS [12]. In addition, the spectra and lifetime of 5 ClMS show that the higher fluorescence of Z results from the attenuation of a radiationless step or steps and not from a change in the radiative lifetime τ_R.

Finally, the fluorescence of 5 ClMSD, which is 90% deuterated at the hydroxyl group, was recorded in cyclohexane solution and showed no measurably isotopic effect in the emission and excitation spectra.

3.3. The fluorescence of methyl 4-methoxysalicylate and methyl 5-methoxysalicylate

Although the emission from 4 MeOMS in the single-collision range is at the limit of sensitivity of our experimental techniques, a dual-band

system similar to that of MS can be seen (Table 1). In the condensed phase in cyclohexane solution the yield is also very low (Table 2) and a spectrum can be obtained only by using long integration times (Fig. 6). The dual-band fluorescence with the characteristic double-maximum excitation spectrum is better resolved than in the parent compound MS under the same experimental conditions. The excitation spectrum of the blue emission at 460 nm closely follows the absorption spectrum, showing that the amount of species IIC responsible for the emission at 323 nm must be very low (less than 1% was estimated for MS in the gas phase in ref. 10).

In 5 MeOMS the first absorption band is strongly shifted to the red compared with the 4-methoxy derivative (Tables 1 and 2). A similar shift, although of lesser magnitude, can be observed in 5 ClMS. The second strong electronic transition, which in these compounds appears in the 250 nm range, shows only a small blue shift. The red shift of the S_1 transition would not be unexpected if the first absorption band contained a sizable contribution from a charge transfer transition.

The striking fluorescence spectra of 5 MeOMS in either the gas phase or cyclohexane departs widely from what is usually observed in salicylic acid derivatives. In this compound an intense single-band emission, with a maximum at 395 nm in non-polar solvents, and an extended long-wavelength tail is obtained (Fig. 7). In fact the fluorescence of 5 MeOMS extends over almost the whole visible spectral range. By integrating the whole band a quantum yield of 0.11 was determined. In the red tail of the fluorescence a change in the slope, and even a very weak shoulder, can be observed at about 490 nm. The shoulder is clearly visible in the fluorescence of the 5-ethoxy derivative [4]. It seems very unlikely that this wide emission band of 5 MeOMS could originate from a single electronic transition. A plausible

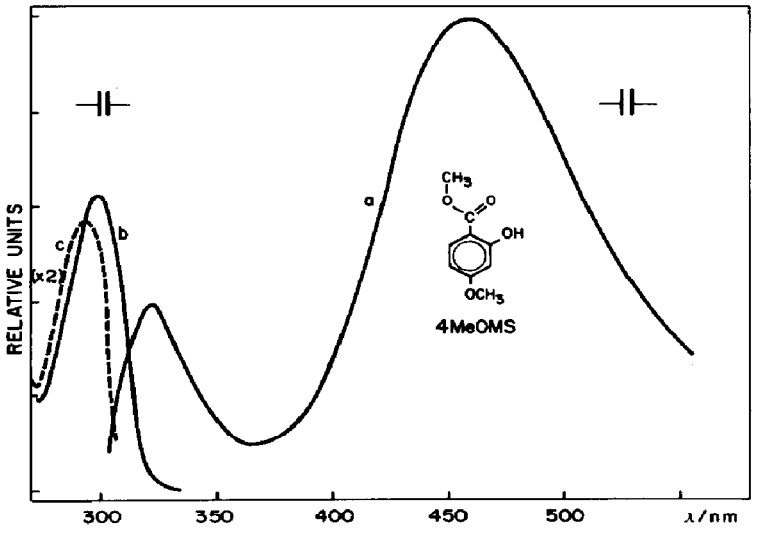

Fig. 6. Fluorescence spectra of 4 MeOMS in degassed cyclohexane: emission recorded at λ_{ex} = 300 nm (curve a); excitation spectrum at λ_{em} = 480 nm (curve b) and λ_{em} = 340 nm (curve c).

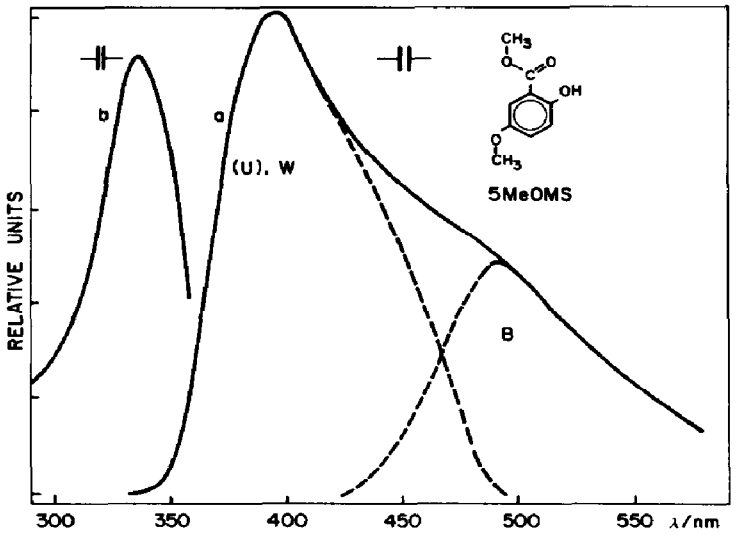

Fig. 7. Fluorescence spectra of 5 MeOMS in degassed cyclohexane: curve a, emission at λ_{ex} = 330 nm; curve b, excitation spectrum at λ_{em} = 460 nm. Details of bands B, W and (U) are given in the text.

explanation is that band B, *i.e.* the proton transfer fluorescence, is concealed in this compound under the much more intense emission at 395 nm. According to this explanation the fluorescence of 5 MeOMS in degassed cyclohexane (Fig. 7) can be decomposed into two partially overlapping bands by subtracting the band B fluorescence of 4 MeOMS shifted to 490 nm from the experimental emission envelope. The gas-phase spectrum of 5 MeOMS, when analysed using the same procedure, gives the same results as those presented in Fig. 7.

The fluorescence excitation spectrum of 5 MeOMS in non-polar solvents is a single band reproducing the absorption spectrum (Fig. 7). A single band with the spike-like shape mentioned before is also recorded in the gas phase (Table 1).

We assigned the emission shoulder at 490 nm of 5 MeOMS and ethyl 5-methoxysalicylate (5 EtOMS) to the fluorescence from the product of the intramolecular proton transfer reaction (Z in Fig. 1). The origin of the intense emission at 395 nm, which is denoted band W here, is unknown. This band can also be observed in dry ethanol and dimethylformamide solutions, as well as in an ethanol solution acidified with trifluoroacetic acid. This last experiment and the gas-phase spectrum indicate that the emission is not phenolate ion fluorescence, which also appears at about 400 nm in several salicyl derivatives.

3.4. The parentage of band W

As has been shown above, three salicyl derivatives substituted at position 5 with electron-releasing groups give rise to a new UV fluorescence band which cannot be associated with the small proportion of species IIC, at least in 5 ClMS. This last statement is not immediately evident in 5 MeOMS

because the fluorescence of IIC molecules is not resolved in the spectrum of Fig. 7 for example. Hence it could be argued that the intense 395 nm band arises from those particular species which are either in a much higher proportion in this compound or alternatively display a very high quantum yield. The first possibility was checked by recording the IR spectra of all the derivatives studied here, because we showed recently [12] that the absorptions at 3470 and 1730 cm^{-1} can be used to ascertain the presence of IIC rotamers. However, no significant differences were observed for the 5-derivatives. The second possibility, an extremely high fluorescence quantum yield of species IIC, would leave unexplained the observation of a single excitation spectrum in 5 MeOMS. In addition, the Stokes shift of the new band W of the 5-derivatives (about 4500 cm^{-1}) deviates substantially from what is found for the IIC emission (2900 - 3500 cm^{-1}) here and elsewhere [12]. Therefore we tentatively postulate that band W, as the blue band B, originates in the excitation of the prevalent species IC with the intramolecular hydrogen bond between the phenol and carbonyl groups which would account for the single excitation spectrum. For some reason the electronically excited IC molecules may survive long enough in 5 ClMS, and much longer in 5 MeOMS and 5 EtOMS, to emit fluorescence, in contrast with MS and all the salicyl derivatives studied to date. It is interesting to recall that this assignment was first proposed 20 years ago by Weller and coworkers to explain the fluorescence of 5 EtOMS and MS [4]. Although our current ideas about the photophysics of MS have changed (see Section 1), it may well turn out that Weller's pioneering hypothesis indeed gives a fair description of the emission from the 5-derivatives!

Finally, if the above assumption is confirmed, it is still necessary to explain the apparent lack of fluorescence from the IIC species in 5 MeOMS (band U). According to the previous discussion of the Stokes shifts, it is very likely that this emission, which is usually weak if present at all, must overlap the short-wavelength edge of the intense 395 nm band. In fact, a consistent 2 nm blue shift of the excitation spectrum of 5 MeOMS (Fig. 7) can be found when the emission wavelength is changed from 460 to 370 nm. However, much higher spectral resolution is needed to give a definitive answer to this question.

4. Conclusions

The electronic excitation of 3 ClMS, 4 ClMS and 4 MeOMS in the gas phase and in non-polar solvents gives rise to a dual-band fluorescence quite similar to that of the parent compound MS. Hence, by analogy, the following assignments were made.

(i) Band B, which appears in the 445 - 475 nm range with a large Stokes shift (more than 10 000 cm^{-1}), is thought to originate from excitation of the dominant molecular species with an intramolecular hydrogen bond between the carbonyl and phenol groups; an excited state proton (or hydrogen) transfer precedes the radiative process.

(ii) The weaker band U (320 - 350 nm) is the fluorescence of a small proportion of rotational isomers where the hydrogen bond links the other ester oxygen with the phenol group [9 - 12]. Therefore no proton transfer reaction occurs in the excited state.

In contrast, excitation of the 5-chloro and 5-methoxy derivatives results in a quite different fluorescence, particularly in the latter compound. A new UV band is recorded (375 - 395 nm) which is the most intense emission in 5 MeOMS and 5 EtOMS. The origin of this band is unknown.

It is suggested here that a third radiative process is taking place in these derivatives, in addition to the other two described above: fluorescence from excited molecules which do not disappear by the proton transfer channel despite having the appropriate hydrogen bond in the ground state. This possibility was considered by Weller and coworkers 20 years ago [4].

Acknowledgments

This work was supported by C.S.I.C. Project 53139-7 and Comisión Asesora de Investigación Científica y Técnica Project 1197-81.

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