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Excited state intramolecular proton transfer and dual emission of the cyclic homo- and heterodimers of 2-hydroxy and 2,6-dihydroxy benzoic acids¹

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Abstract

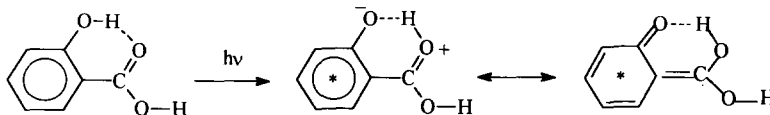
The fluorescence and excitation spectra of homo- and heterodimers formed by salicylic and 2,6-dihydroxy benzoic acids (SA and DHBA respectively) with various carboxylic acids were obtained in the crystalline state, liquid and frozen glassy solutions within the temperature range 300–90 K. In all the cases, dual emission has been found with the low frequency band attributed to the excited state with intramolecular proton transfer (ESIPT) and the high frequency one to a state without ESIPT. The relative intensities of these bands depend strongly on the temperature, excitation wavelength and the pK_a value of the second acid molecule involved in a cyclic dimer. The dual emission of molecules like methyl salicylate is conventionally explained in terms of the ground state tautomeric equilibrium with the $OH \cdots OH$ intramolecularly hydrogen bonded isomer incapable of ESIPT. Since in the case of 2,6-dihydroxy benzoic acid the only stable isomer with two hydrogen bonds can exist, this explanation seems to be at least insufficient. Other explanations of the dual emission origin are discussed. An attempt is made to explain the available experimental data using the hypothesis involving double well potential surface of the cyclic dimer in the excited state. In the framework of this hypothesis, the barrier between two wells emerges from the reorganization of the whole hydrogen bonded system of a dimer.

Keywords: Hydrogen bonding; Fluorescence spectroscopy; Excited state proton transfer; Salicylic acid; 2,6-Dihydroxy benzoic acid

1. Introduction

In the pioneering works of Weller [1,2], the anomalously large Stokes shift was found in fluorescence spectra of molecules like salicylic acid

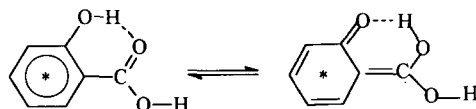
and its derivatives characterized by a strong intramolecular $OH \cdots O=C$ hydrogen bond. This fact was explained by existence of excited state intramolecular proton transfer (ESIPT) reaction with formation of zwitterionic (quinoic) form:



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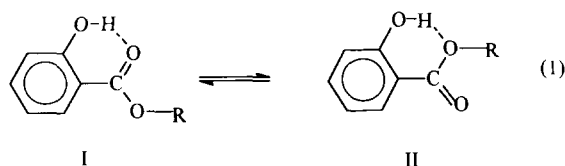
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In some cases the “dual emission” (the UV and blue fluorescence simultaneously) has been detected and interpreted in terms of the excited state equilibrium between the benzoic and quinoic forms of the molecule:



The quinoic tautomer formed by the excited state intramolecular proton transfer is responsible, in this treatment, for the blue fluorescence showing an anomalously large Stokes shift, while the benzoic form without ESIPT gives the UV emission with a normal Stokes shift.

Further, experimental studies were performed



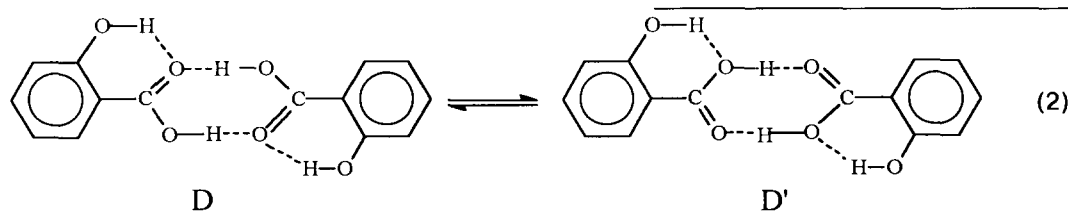
mainly with methyl salicylate, salicylaldehyde and similar molecules [3–13], where the spectral picture is not complicated by effects of strong intermolecular hydrogen bonding important in the case of SA. Now, in most of the published papers [6–10] the dual fluorescence of methyl salicylate is interpreted as a manifestation of the ground state rotameric equilibrium (1) shifted strongly to rotamer

undergoes the complete ESIPT leading to the blue fluorescence.

For solutions of SA in aprotic solvents, the intensity of the UV component (without ESIPT) has been found to be anomalously high and increases with concentration. The supposition was made that this is connected with dimerization of SA [3,14].

In [15] it was shown that the emission spectrum of the crystalline SA (consisting of cyclic dimers, [16]) reveals a doublet with the sub-band relative intensities depending strongly on the temperature and, in contrast to the case of monomer molecules and methylsalicylate, on the excitation wavelength. The explanation of these results, suggested in [15], is based on the concept of ground state equilibrium (2) similar to (1), between two tautomers of the cyclic dimer, the D' tautomer with OH...OH intramolecular hydrogen bonds being assumed to be energetically more stable.

In contrast to the case of monomeric SA, the transformation between D and D' tautomers is able to proceed via the double proton transfer with the characteristic time which may be close to the excited state life time. Thus, the relation between the UV and blue bands is affected not only by temperature dependence of the equilibrium constant (2), but also by the rate of the double proton transfer. The authors [15] believe that the double proton transfer barrier can be overcome using the excessive vibrational energy arising from the high frequency excitation, which might be responsible for the observed dependence of the excitation wavelength.

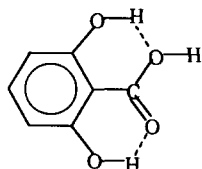


I. As it involves the breaking of a strong intramolecular hydrogen bond, this equilibrium cannot be fast enough to accomplish this during the excited state life time (1–10 ns). Thus, ESIPT cannot take place in the excited state of rotamer II giving rise to the UV emission band, while the usual rotamer I

However, the concept of the ground state equilibrium (2) shifted to the D' rotamer is in strong contradiction to the neutron diffraction study of crystalline SA [16], which shows the existence of the OH...O=C intramolecular hydrogen bond only, as well as to results of IR

and low temperature NMR investigations of the dissolved SA [17,18]. In the latter papers, no measurable content of the D' tautomer was found.

From this point of view, the 2,6-dihydroxy benzoic acid molecule (DHBA) seems to be of



special interest. NMR study of this acid [17,18] shows the existence of the fast (in the NMR scale) degenerate equilibrium between two equivalent tautomers involving the double proton transfer. In terms of the above mentioned rotameric concept, there should be no dual emission in the case of DHBA cyclic dimer, since both its tautomers are capable of ESIPT.

The goal of the present work is a parallel investigation of the fluorescence spectra of SA and DHBA under conditions of their full (or almost full) dimerization, i.e. at the temperature lower than 200 K. The influence of the temperature, excitation wavelength and the acid-base properties of the molecules involved in cyclic dimerization has been examined. For the latter purpose, mixed cyclic dimers of SA and DHBA with several carboxylic acids of different pK_a have been studied.

2. Experimental

The fluorescence and fluorescence excitation spectra were recorded on a Hitachi M-850 fluorimeter and SFL-2 instrument with two double monochromators and the emission registration in the pulse counting regime. The temperature was maintained and measured in the range 90–300 K using a modified JASCO CRY-1B optical cryostat. IR and UV absorption spectra were recorded on the Hitachi 270-30 and Zeiss (Jena) Specord M-40 instruments.

SA and DHBA were purchased from Fluka and used without purification. Isooctane and methyl cyclohexane for UV spectroscopy (Merck) were used as solvents.

3. Results and discussion

3.1.

Fluorescence spectra of strongly diluted solutions ($\leq 10^{-5}$ mole l^{-1}) of SA in aprotic low dielectric solvents at the room temperature, when monomer–dimer equilibrium is shifted almost completely to monomers (as being shown by IR measurements), independently of the excitation wavelength, reveal the intensive band with Stokes shift about 150 nm and maximum in the blue region — near 430 nm (Fig. 1, curve b). Obviously, this band corresponds to the main component of emission of SA monomers, resulted from an ESIPT process similar to that observed for methyl salicylate or salicylaldehyde molecules¹.

With increase of concentration or with temperature decrease, when essential amounts of dimers appear, the band in UV region (near 370 nm) typical for emission of the form, where no ESIPT takes place, arises (Fig. 1c). The spectrum of polycrystalline SA, which is known to consist of cyclic dimers only [16], recorded with 300 nm excitation, looks like a doublet with comparable intensities of UV and blue components (Fig. 1d). A similar doublet is observed also for solutions at the temperatures below 200 K and concentrations $\sim 10^{-4}$ mole l^{-1} , when the content of monomers is negligible, and detected spectra represent practically pure emission of cyclic homodimers (Fig. 2).

The relative intensities of blue and UV components of this doublet band depend on the temperature and excitation wavelength. Thus, in the case of 10^{-4} mole l^{-1} solution of SA in isooctane/methylcyclohexane mixture at 168 K and excitation at 340 nm, the intensities of both components are comparable (Fig. 2b). If the temperature is decreased down to 90 K, the blue component becomes stronger, and the UV weaker. (Similar changes are observed in the spectrum of the polycrystalline sample). The use of the shorter excitation wavelength — 290 nm instead of 340 nm — at

¹ The weak emission in the UV region, which is also detected usually under such conditions, is caused mainly by traces of dimers. However a more detailed study of monomer fluorescence is of special interest and the results will be published elsewhere.

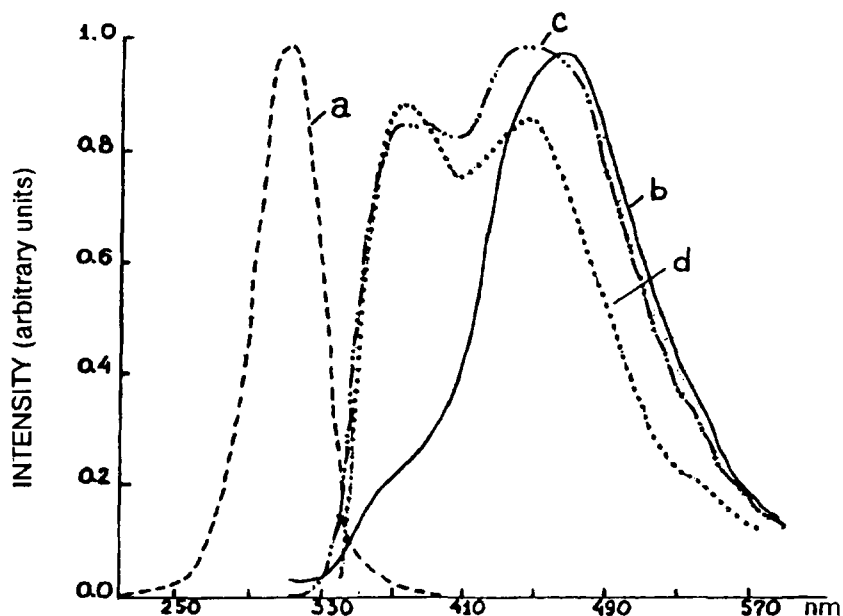


Fig. 1. Absorption (a) and fluorescence (b, c) spectra of SA solutions in CCl_4 : a, b, $10^{-5} \text{ mol l}^{-1}$; c, $4 \times 10^{-4} \text{ mol l}^{-1}$; d, fluorescence of solid SA; $\lambda_{\text{ex}} = 300 \text{ nm}$.

the fixed temperature also leads to weakening of the UV band (Fig. 2a). At 90 K its intensity is reduced almost to zero.

Excitation spectra of the same solutions at 90 K (Fig. 2c) exhibit the doublet structure with red edge maximum, when the registration at 370 nm is used, and with close intensities of components with 460 nm registration.

3.2.

Spectra of the mixed dimers formed by SA with other carboxylic acids also reveal the dual fluorescence, the relative intensities of the blue and UV bands being dependent on pK_a of the acid molecule used as a partner. Intensity of UV emission becomes greater with decrease of pK_a value of a partner and vice versa.

For example, fluorescence and fluorescence excitation spectra of $10^{-4} \text{ mole l}^{-1}$ SA solutions in isooctane, containing a great excess ($5 \times 10^{-1} \text{ mole l}^{-1}$) of trichloroacetic acid are presented in Fig. 3. Using the constant of the mixed dimerization, estimated with the help of IR or NMR data (see [19], for example) one can find

that the most part of SA molecules is bonded in heterodimers. Under these conditions, only the UV fluorescence band is observed upon the red edge (340 nm) excitation within the whole temperature range (Fig. 3a). Hence, ESIPT is hampered by dimerization. Only with short wavelength excitation blue fluorescence can be observed near 440 nm. As in the previous case, its intensity increases with temperature decrease (Fig. 3b). Correspondingly, the excitation spectrum at 90 K displays a maximum near 290 nm with registration at 375 nm; with 460 nm registration the maximum is shifted to 340 nm (Fig. 3c).

If trimethylacetic acid, which is weaker than SA ($\text{pK}_a = 5.05$), is used as a partner, the blue component becomes stronger compared with the homodimer in the same conditions. However, the UV component can be detected with the long wave excitation; character of the temperature dependence of the components intensities ratio is the same as in previous cases.

3.3.

Fluorescence spectra of 2,6-dihydroxy benzoic

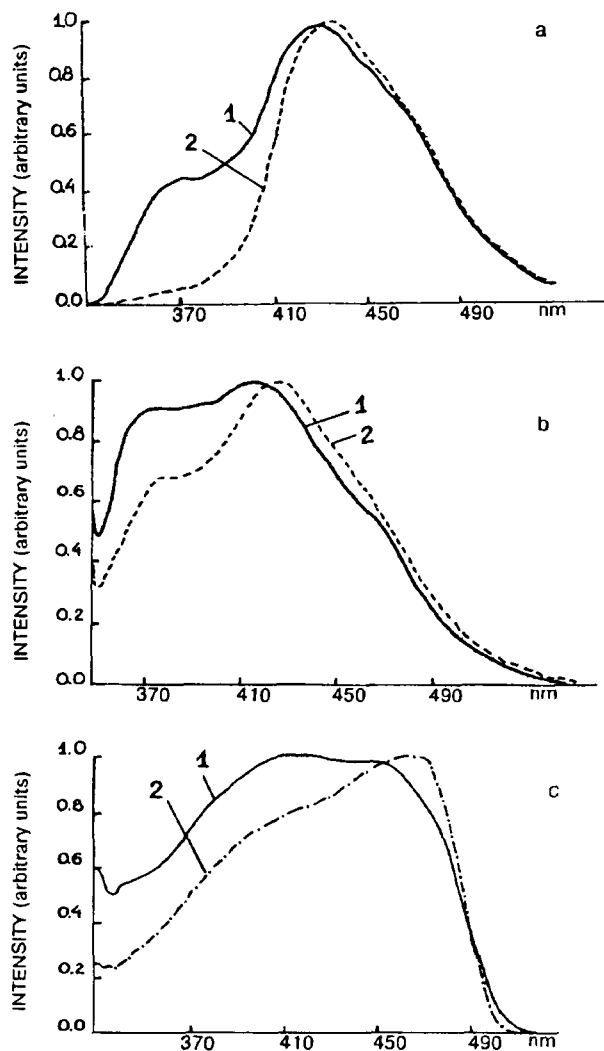


Fig. 2. Fluorescence (a, b) and fluorescence excitation (c) spectra of SA solutions (10^{-4} mol l^{-1}) in iso-octane methylcyclohexane mixture: (a) $\lambda_{ex} = 290$ nm; (b) $\lambda_{ex} = 340$ nm (1, 168 K; 2, 90 K); (c) 90 K, $\lambda_{em} = 460$ nm (1), 370 nm (2).

acid, both in solutions and in the solid state, reveal the same peculiarities, which have been described for SA.

Fig. 4a shows the concentration dependence of the fluorescence spectrum of DHBA solution in hexane with excitation at 330 nm. It is seen that at low concentrations, when monomers dominate, only blue emission band near 470 nm is observed practically, confirming that excitation of the free

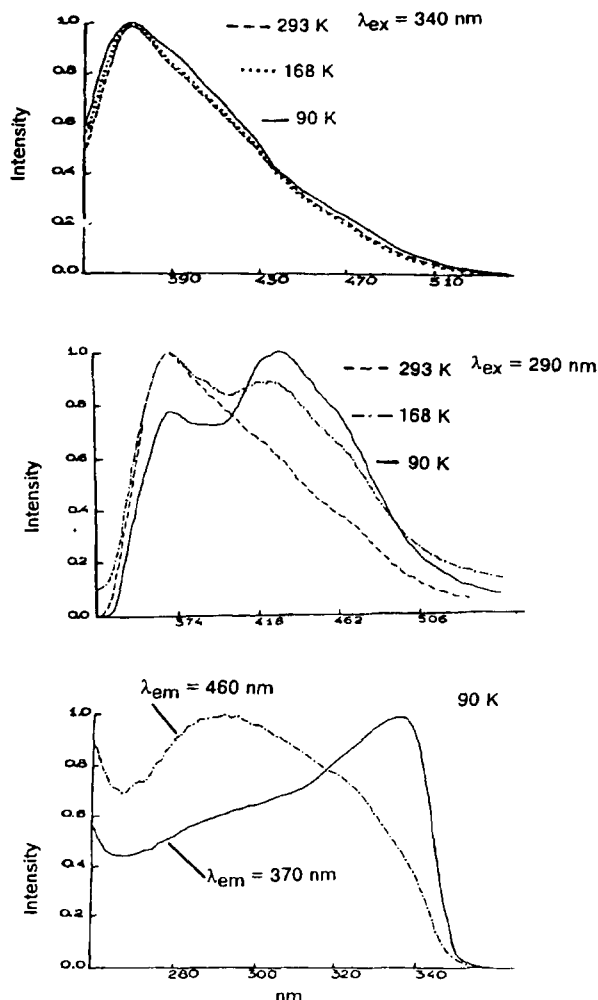


Fig. 3. Fluorescence (a, b) and fluorescence excitation (c) spectra of SA solutions (10^{-4} mol l^{-1}) in iso-octane in presence of 5×10^{-1} mol l^{-1} of trichloroacetic acid.

molecule is followed by ESIPT reaction. The increase of concentration (and, correspondingly, of relative content of the dimers) is accompanied by appearance and increase of the UV band near 410 nm, while the blue band almost disappears. Figs. 4b and 4c illustrate, respectively, the enhancement of the blue component with shortening of the excitation wavelength in spectrum of solution containing mixed dimers DHBA — monochloroacetic acid and with temperature decrease for the case of crystalline DHBA — trichloroacetic acid dimers.

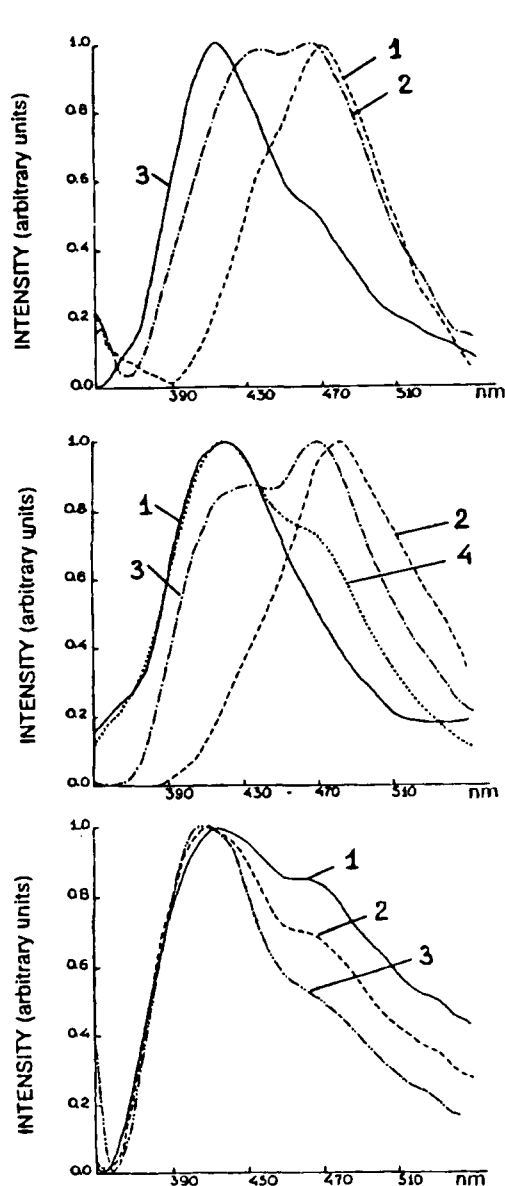


Fig. 4. Fluorescence spectra of 2,6-dihydroxybenzoic acid. (a) Solutions in hexane 2×10^{-6} (1); 6×10^{-4} (2) and 5×10^{-3} (3) mol l^{-1} ; $\lambda_{\text{ex}} = 330$ nm. (b) Mixed dimers with trichloroacetic acid (polycrystalline sample); (1) 305 K, (2) 80 K, (3, 4) intermediate temperatures; $\lambda_{\text{ex}} = 310$ nm. (c) Solution (5×10^{-6} mol l^{-1}) in CCl_4 in presence of 5×10^{-2} mol l^{-1} of monochloroacetic acid, 290 K; $\lambda_{\text{ex}} = 320$ (1), 330 (2), 350 (3) nm.

a 3.4.

The discovery of the dual emission in the case of DHBA, when no rotameric equilibrium exists in the ground state, leads to conclusion that similar emission of SA dimers also hardly can be explained by ground state equilibrium (2). Therefore another explanation of the dual fluorescence origin, which would be applicable for both the acids is required. Some approaches for treating this problem follow.

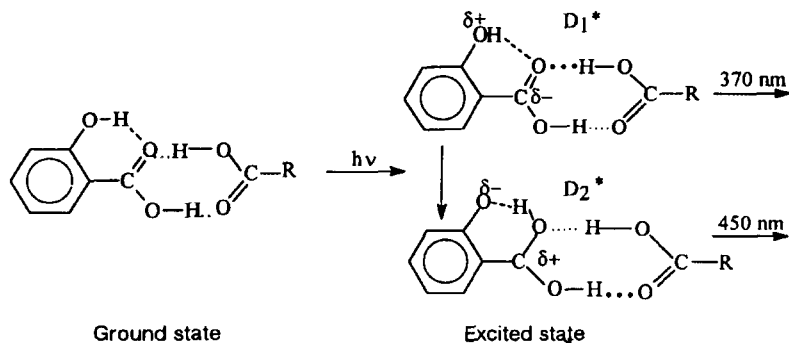
(a) It seems reasonable to consider the possibility of formation of two different configurations (and, correspondingly, of two minima on potential surface) in the excited state.

As was mentioned above, the concept of the excited state double well potential has been proposed initially in Weller's works [1,2]. The presence of dimers was not taken into account in these works; results were treated as if the double fluorescence observed was emitted by monomer molecules. Later, when the investigations (both experimental and theoretical) of methylsalicylate, salicylaldehyde and other molecules similar to SA monomer did not confirm the presence of two minima in the excited state, this concept was doubted [6–10]² and attention focused on the rotameric equilibrium in the ground state. However, in fact, the dual fluorescence of SA, found by Weller, at least in aprotic solvents at low temperatures, should be attributed to SA dimers, which dominate under such conditions. Hence, peculiarities of cyclic dimers structure should be taken into account.

The simplest model, where double well excited state potential surface appears as result of these peculiarities, seems to be the following.

Existence of pronounced potential minimum corresponding to benzoic form in the excited state seems to be more probable for SA molecule involved in a dimer than for monomer because the intramolecular H-bond becomes weaker in the dimer due to effect of intermolecular H-bonding.

² When this paper was in press, the paper by Bisht et al. appeared (P.B. Bisht, H. Petek, K. Yoshihara, U. Nagashima, J. Chem. Phys., 1995, v. 103 (13), P. 5290), where the dual emission of the rotamer I of the monomeric SA is reported to have been detected and explained in terms of the excited state tautomerization.



Excitation of one molecule in cyclic homodimer affects sharply the symmetry of the dimer, since one of intermolecular H-bonds becomes stronger, while the other one weaker. Corresponding configuration of the dimer is designated as D_1^* .

Intramolecular proton transfer in the excited molecule changes the charges located on carboxylic group. This involves the reorganization of the whole hydrogen bonded system of the dimer, when strong intermolecular bond becomes weaker and vice versa (configuration D_2^*). Ultraviolet and blue fluorescence bands correspond to emission of D_1^* and D_2^* forms respectively.

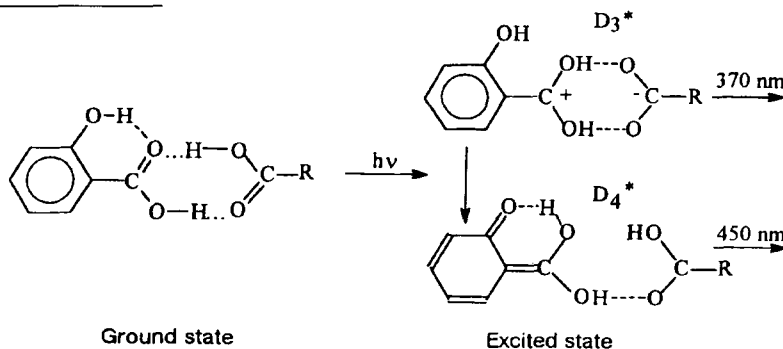
Thus, the proton transfer is accompanied by the essential change of dimer geometry, which can probably determine the existence of a barrier between the potential wells of configurations D_1^* and D_2^* .

The experimentally observed excitation wavelength dependence can be explained in the framework of this scheme, if one supposes that the barrier is rather high and the probability of tunnelling is negligible. Then the appearance of the blue emission at low temperatures can be detected only with the excitation wavelength short enough to excite the

levels lying above the top of the barrier. In other words, it is implied that proton-transfer form D_2^* is more stable thermodynamically, but its formation is hampered kinetically. Since the temperature decrease leads to enhancement of the blue fluorescence, one can conclude that the minimum corresponding to proton-transfer configuration D_2^* is deeper. However, the relative populations of D_1^* and D_2^* -states, which determine the intensities of the short and long wave emissions, are not equal to thermodynamically equilibrated, being dependent on the excitation wavelength and on the relative rates of proton transfer and vibrational relaxation processes.

Since the cyclic homodimer, containing only one excited molecule, becomes asymmetric, there is no principal difference between excited homo- and heterodimers within the considered model; only the changes of the excited state potential surface parameters (relative depth of the wells, height of the barrier), depending on pK_a values of the acids forming the dimer, take place.

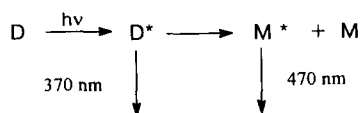
(b) One can suggest another pair of tautomeric structures of the excited cyclic dimer:



Here the structure D_3^* , formed as result of intermolecular ESIPT, is assumed to be responsible for the appearance of the short wave emission. The possibility of formation of such an ionic-pair structure of the excited cyclic dimer has been suggested earlier [20] as applied to intermolecular ESIPT in naphthoic acid. Existence of the barrier, as well as temperature and wavelength dependencies of the dual emission, can be explained in the framework of this model similarly to the previous case.

In order to discriminate between two considered versions of the double well excited state potential, the changes of the relative intensities of blue and UV components in fluorescence spectra of SA with changes of solvent polarity were studied. It has been found that the increase of polarity in a series of aprotic solvents (hexane, CCl_4 , CH_2Cl_2) leads usually to the increase of the blue component. This seems to be an argument rather in favour of the first scheme, since in this case more polar structure is responsible for blue emission.

(c) The other approach to an explanation of the dual emission, which can be taken into consideration, is based on the assumption of the photo dissociation of the dimer. According to this idea, the long wave excitation of the dimer does not provide ESIPT reaction and hence gives rise only to UV emission. If the excitation energy is high enough, the dissociation of the cyclic dimer takes place with consequent emission of blue fluorescence by one of monomers formed due to the dissociation:



This model is capable of explaining the excitation wavelength dependence of dual emission, but the origin of the temperature dependence observed remains unclear. The presence of the blue component in the spectra of the rigid glassy samples also seems to be an argument against this model.

4. Conclusions

The results obtained show that dual fluorescence with blue and UV components corresponding

to emission of some forms with and without intramolecular proton transfer, as well as its specific temperature and excitation wavelength dependence, are typical for cyclic homo- and heterodimers formed by both salicyclic and di-ortho-hydroxy benzoic acids. The main conclusion, which can be drawn from this fact, is that the ground state tautomeric equilibrium (2) cannot be responsible for these phenomena in the systems studied.

An attempt was made to find a more suitable explanation of the dual fluorescence origin, taking into account structural peculiarities of the cyclic dimer. A self-consistent interpretation of the experimental data can be obtained when supposing that the excited state of the dimer is characterized by a double well potential surface with rather high barrier between two wells, arising from reorganization of the dimer geometry upon ESIPT process. However this hypothesis, as well as others mentioned, needs further analysis. Particularly, the ab initio calculations of potential surfaces of monomers and dimers in the ground and excited states are of great interest. It seems also that validity of discussed models can be verified experimentally by high time resolution measurements.

Acknowledgement

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