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Conformational effects in excited state intramolecular proton transfer of organic compounds

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Abstract. The results of investigations of excited state intramolecular proton transfer of organic fluorophores with various intramolecular hydrogen bonds are analyzed. The efficiency and mechanism of these reactions and, therefore, spectral luminescent characteristics of these fluorophores are determined to a greater extent by the conformational equilibrium of rotamers in the ground electronic state. The results of femtosecond absorption and time-resolved fluorescence spectroscopy point out that in six-membered complexes with strong intramolecular hydrogen bond, the excited state intramolecular proton transfer is barrierless, has a rate constant of $\sim 10^{13}$ s^{-1} and it is a non-equilibrium process. In the compounds with weaker intramolecular hydrogen bond, the existence of potential barrier results in the decrease in excited state intramolecular proton transfer rate constant by 2 – 3 orders of magnitude. The bibliography includes 232 references.

I. Introduction

The absorption of light by an organic compound the molecules of which contain a heteroatom (N, O, S) connected to an aromatic ring induces a change in the charge localized on the heteroatom; as a result, the acid-base properties of the organic molecule change. Experimental facts pointing out the change in the acid – base properties upon photoexcitation have long been known. Back in 1931 Weber [1] discovered the change in the fluorescence spectrum of 1-naphthylamine 4-sulfonate upon variation of the solution acidity, while the absorption spectrum remained invariable. Forster [2] attributed this phenomenon to the change in the acid-base properties of molecules in the excited state. Later, the problem of acid – base properties of electronically excited molecules and excited state proton transfer were studied in detail by Weller.[3]

The proton donor and proton acceptor groups may be located either in different molecules (excited state intermolecular proton transfer) or in the same molecule [excited state intramolecular proton transfer (ESIPT)]. The excited state intermolecular proton transfer occurs by a dynamic mechanism (the process rate is determined by reactant diffusion toward each other) or by a static mechanism in the pre-formed hydrogen-bonded complex.[4] The excited state intramolecular proton transfer occurs in an intramolecular hydrogen-bonded complex by a static mechanism. The phenomenology and the mechanism of ESIPT have been considered in reviews,[5 – 11] the latest of which was published in 2000. The extensive knowledge of ESIPT accumulated to date requires analysis of new experimental data and formulation of general trends of this process. It is noteworthy that publications of the last decade emphasize more and more often the crucial role of conformational processes in ESIPT systems. A substantial role is played by the conformational processes involving species in the ground electronic state. This is typical of molecules existing as two (or more) rotamers of which only one can form intramolecular hydrogen bond, which is a necessary condition for proton transfer. In this case, interconversion of rotamers rather than the proton transfer elementary step is the factor determining the proton transfer rate. This review considers the conformational effects in the ESIPT, the influence of the conformational equilibrium of molecules in the ground electronic state on the efficiency, the mechanism, and the kinetics of ESIPT.

Excited state proton transfer takes place in the molecules of aromatic compounds that contain a proton-donor (–OH or –NH) and a proton-acceptor (O=C< or N<) functional groups located in the *ortho*-positions relative to each other. Four types of intramolecular hydrogen bonds can exist in such molecules:

O – H···O=C<, O – H···N<, N – H···N<, N – H···O=C<.

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The ESIPT reactions are considered according to this classification.

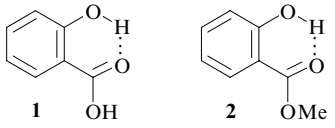
II. Excited state intramolecular proton transfer in hydrogen-bonded complexes of organic OH acids

1. O–H···O=C< bonded complexes

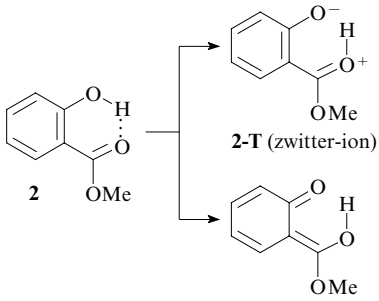
The hydrogen bond in these complexes is strong. This is the case for numerous aromatic molecules that contain hydroxy and carbonyl groups in the *ortho*-positions to each other.

a. Aromatic hydroxy acids, hydroxy aldehydes, hydroxy ketones and their derivatives

The ESIPT was first found for salicylic acid (**1**) and methyl salicylate (**2**).



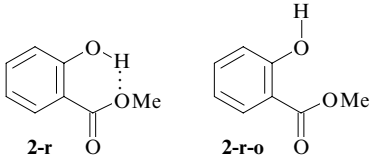
In a solution of methyl salicylate, Marsch [12] observed two fluorescence bands, in the UV and in blue spectral regions. Later, Weller [3] interpreted these two bands as the emission bands of the starting excited molecule and the tautomerization product in the excited state, which occur in equilibrium.



He assumed that the activation energy of ESIPT is less than 10 kJ mol^{-1} and that the tautomer formed can be represented as a zwitter-ion structure.[13] In the case of equilibrium of tautomers in the excited state, two minima are assumed to exist in the proton transfer potential curve.

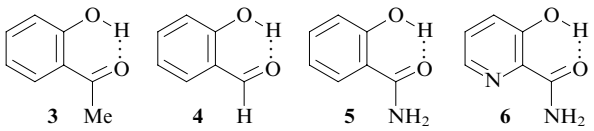
The subsequent studies showed that Weller's interpretation was erroneous. The tautomer emission was observed at very low temperatures in supersonic jet flows,[14–20] in neon matrix [21] and in solid durene.[15] Even at 4 K the rate of proton transfer was very high. Femtosecond investigations of the gas phase fluorescence at room temperature showed that the proton transfer occurs within 60 fs and that the tautomer is better described by a neutral than by a zwitter-ion structure.[22] These results together with the fact that the excitation spectra of the two emission bands are not identical (known experimental fact) are inconsistent with the presence of two minima in the proton transfer potential curve. Sandros [23] was the first to assume the existence of an equilibrium between the hydrogen-bonded intramolecular complex and a species without hydrogen bond even in the ground electronic state. The excitation of hydrogen-bonded intramolecular complex results in ESIPT. This assumption was later confirmed.[24–26] Currently it is considered that several conformers are responsible for the bands in the fluorescence spectrum of methyl salicylate.

Excited state proton transfer in structure **2** with a hydrogen bond between the hydroxy group and the carbonyl oxygen atom occurs without overcoming a potential barrier to give the tautomer. This is confirmed by the lack of isotope effect (OH/OD) in the buildup kinetics of the fluorescence of the tautomer.[16,20] One more point in favour of the barrierless type of the reaction is the fact that two-band fluorescence of salicylic acid arising after excitation of only one rotamer was observed in supersonic jet flows for all excitation energies.[18] The fluorescence intensity ratio in the blue and UV regions was lower for higher excitation energies. An opposite picture would have been observed for a potential curve with two minima. For a curve with one minimum, the low-energy excitation corresponds to a non-vertical transition in which the proton transfer form is directly populated. An increase in the excitation energy results in an increase in the Frank–Condon factor for emission in the UV range. Another hydrogen-bonded form (**2-r**) does not undergo ESIPT and emits 'normal' UV fluorescence.



The existence of rotamers **2** and **2-r** was confirmed by matrix isolation spectroscopy experiments.[27] The third structure (**2-r-o**), so-called open structure without an intramolecular hydrogen bond, contributes to short-wavelength emission.[23,26]

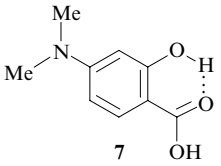
In a protic solvent, ESIPT can be affected by the presence of intermolecular hydrogen bonds. Under certain conditions, the formation of cyclic dimers of salicylic acid is possible, in which the double proton transfer is confirmed by experiment.[18–28] Similar results were obtained for other salicylic acid derivatives.[9,29] The interpretation of the results is similar to that for methyl salicylate: two different species in the ground state are responsible for fluorescence in the blue and UV spectral regions. For compounds that can form only one closed conformer with an intramolecular hydrogen bond such as *o*-hydroxyacetophenone (**3**), *o*-hydroxybenzaldehyde (**4**), salicylamide (**5**) and 3-hydroxypicolinamide (**6**), no UV fluorescence in solution was observed.[30–34]



This attests to the absence of an open conformer analogous to **2-r-o**. However, the open conformers of molecules **3**–**5** are formed on irradiation in low-temperature inert gas matrices.[26,35,36]

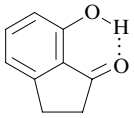
Excited state intramolecular proton transfer in 4-dimethylaminosalicylic acid (**7**) in an aqueous cyclodextrin solution was responsible for three fluorescence bands caused by emission of the locally excited state of the initial form, the tautomer resulting from ESIPT, and the intra-

molecular charge transfer (ICT) excited state. After ESIPT, the efficiency of formation of the ICT state considerably increases.[37]



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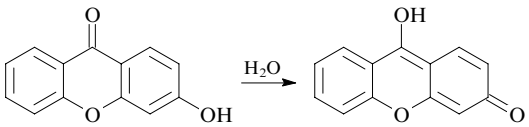
The excited state intramolecular proton transfer in *o*-hydroxyaldehydes and *o*-hydroxy ketones was first studied in relation to *o*-hydroxyacetophenone and *o*-hydroxybenzaldehyde.[38] The major species existing in non-polar solvents are closed conformers with intramolecular hydrogen bond. On exposure to light, excited forms of these conformers with transferred proton are formed. In alcohol solutions, the major species are open conformers with intermolecular hydrogen bonds. In alcohol solutions, hydroxybenzaldehyde exhibits two-band fluorescence spectra. The first band is due to fluorescence of the closed conformer of the enol form and the second one is attributable to the open solvated conformer. The relatively low ESIPT rate is due to the $n-\pi$-character of the S_1 state. The excited state keto–enol tautomerism was observed for methyl salicylate, *o*-hydroxyacetophenone, salicylamide and 7-hydroxyindan-1-one (**8**) in crystalline durene and in supersonic jet flows.[14]



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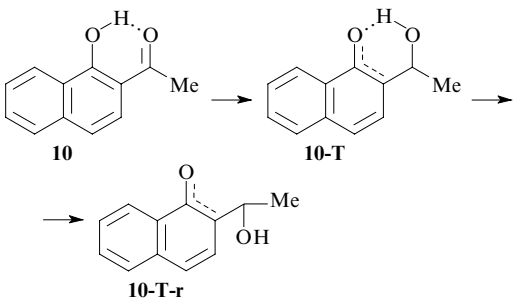
For none of these compounds, two minima on the potential energy surface were found.

In 3-hydroxyxanthen-9-one (**9**), the formal excited state proton transfer takes place through water molecules to give the corresponding *p*-quinonemethide (**9-T**).[39]



9 **9-T**

Calculations showed the existence of photoinduced internal rotation processes and ESIPT followed by the internal rotation in the 2-acetyl-1-hydroxynaphthalene (**10**) molecule in the excited state.[40]

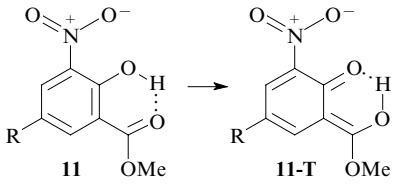


10 **10-T** **10-T-r**

According to calculations, there are several minima on the potential energy surface; the energy barrier to ESIPT is 5.49 kcal mol^{-1}. The internal rotation in molecule **10-T** with an activation energy of 7.53 kcal mol^{-1} produces more stable form **10-T-r**. The crucial role in the excited state proton transfer dynamics is played by the in-plane and out-of-plane vibrations in the hydrogen bonded complex **10**. In neutral aqueous solutions, the enol form of compound **10** undergoes ESIPT, which brings about the internal rotation in the resulting keto tautomer (**10-T**) over a period of tens of picoseconds to give the excited rotamer (**10-T-r**). The lifetime of this rotamer is several nanoseconds.[41]

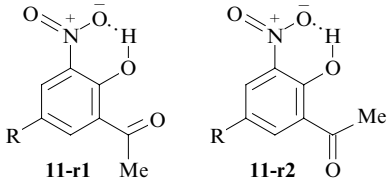
In cyclodextrin solutions, the internal rotation dynamics changes considerably. As the size of the cyclodextrin cavity decreases, the isomerization channel resulting in **10-T-r** is closed, and fluorescence emission of **10-T** is observed. As the cavity size increases, the fast component of the emission anisotropy of the complexes becomes shorter and the slow component becomes longer. The formation of **10-T-r** was demonstrated experimentally based on the dependences of the fluorescence of the ESIPT product on the solvent viscosity and polarity.[42] In the series of alcohols, the rate constant for the radiationless deactivation increases upon an increase in the solvent polarity. For aprotic solvents, an opposite dependence is observed.

For 2-hydroxy-5-methyl-3-nitroacetophenone and 5-chloro-2-hydroxy-3-nitroacetophenone, the hydrogen bonded enol form (**11**) in the ground state is in thermal equilibrium with conformers **11-r1** and **11-r2** formed upon torsional rotations.



11 **11-T**

R = Me, Cl.

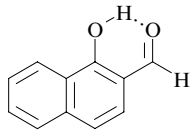


11-r1 **11-r2**

R = Me, Cl.

In non-polar aprotic solvents, compounds **11** in the excited state undergoes ESIPT, fluorescence of the keto conformer **11-T** with anomalous Stokes shift is observed, and conformers **11-r1** and **11-r2** emit fluorescence with a normal Stokes shift.[43] In protic and polar solvents (ethanol and acetonitrile), the equilibrium of enol conformers in the ground state sharply shifts toward form **11**. Therefore, in these solvents only fluorescence of the keto conformer **11-T** is observed.

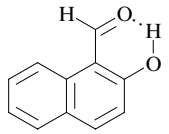
The fast ESIPT was found for *o*-hydroxynaphthaldehydes. The excitation of the closed conformer with intramolecular hydrogen bond of 1-hydroxy-2-naphthaldehyde (**12**) in solvents of different polarity affords excited keto conformer, as indicated by the appearance of a long-wavelength band in the fluorescence spectrum.[44]



12

The results of calculations confirm the occurrence of a barrierless ultrafast excited state proton transfer in the hydrogen-bonded intramolecular complex.

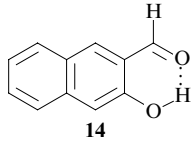
In the case of 2-hydroxy-1-naphthaldehyde (**13**), the excitation of the open and closed conformers accounts for the presence of two bands in the fluorescence spectrum.[45]



13

The short-wavelength band corresponds to fluorescence of the open conformer, while the long-wavelength band corresponds to the fluorescence of the zwitter-ion formed upon ESIPT of the closed conformer. Deprotonation is markedly retarded in neutral and anionic micelles compared with cationic ones. The increase in the fluorescence intensity of the anion in cationic micelles was attributed to the presence of hydroxide ions in the local environment.[46] The fluorescence intensity of the anion decreases in anionic micelles as a result of formation of the conformer with more effective radiationless deactivation.

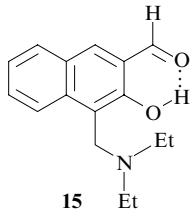
The 3-hydroxy-2-naphthaldehyde (**14**) molecule can exist, depending on the solvent, as open or closed form or as a complex hydrogen-bonded to the solvent.[47]



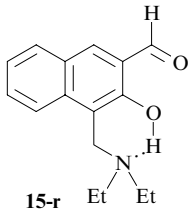
14

The excited state proton transfer in molecule **14** gives the excited keto tautomer with a very low fluorescence quantum yield (6.8×10^{-6} in cyclohexane).[48]

The 4-diethylaminomethyl-3-hydroxy-2-naphthaldehyde (**15**) molecule contains two competing sites forming hydrogen bond, namely, $O-H\cdots O=C<$ and $O-H\cdots NR_2-$; therefore, in the ground state, conformers of two types are formed, **15** and **15-r**.[48]



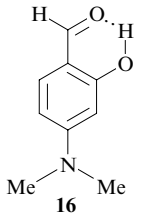
15



15-r

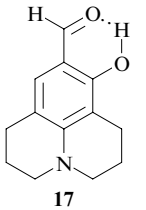
These conformers undergo ESIPT to give the excited zwitter-ion (from **15-r**, fluorescence maximum at 485 nm) and the excited keto tautomer (from **15**, fluorescence maximum at 730 nm). The excited state proton transfer is a very fast (< 150 fs) and almost barrierless process, as it does not depend on the replacement of OH by the OD group.

On excitation of 2-hydroxy-4-dimethylaminobenzaldehyde (**16**) in various solvents, both charge transfer and intramolecular proton transfer take place.[49] The quantum chemical calculations showed that both processes are barrierless.



16

Upon excitation of the 8-hydroxy-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*i*,*j*]quinolizine-9-carbaldehyde (**17**) molecule, both ESIPT and charge transfer are possible; in the closed conformer, only ESIPT takes place.[50]

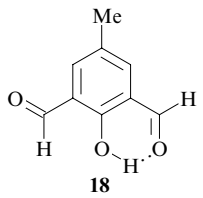


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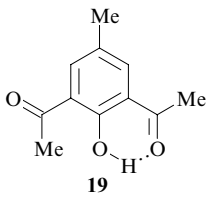
In non-polar solvents, only fluorescence with anomalous Stokes shift of the proton transfer conformer is observed. In polar solvents, this fluorescence band is accompanied by short-wavelength fluorescence, which was assigned to emission of the open solvated form.

The effect of substituents on the ESIPT of *o*-hydroxybenzaldehyde was discussed using the nodal-plane model proposed by the authors.[51] A femtosecond pulse photolysis study of the excited state proton transfer and internal conversion (IC) in molecule **4** showed that ESIPT is the ballistic motion of well-confined wave packet along the skeletal coordinates of a hydrogen bonded ring.[52] The internal conversion is a thermally activated process with an energy barrier of ~0.2 eV caused by crossing of the $\pi-\pi^*$ and $\pi-\sigma^*$states. The coordinates involved in the ESIPT and IC are orthogonal.

The rate constants for the ESIPT in 2,6-diformyl-4-methylphenol (**18**) and 2,6-diacetyl-4-methylphenol (**19**) equal to $(4-5) \times 10^{12}$ s^{-1} are lower than the corresponding constants for other compounds, which is attributable to a considerable skeletal rearrangement needed for proton transfer.[53] The ESIPT is followed by fast intramolecular vibrational relaxation on the picosecond time scale.



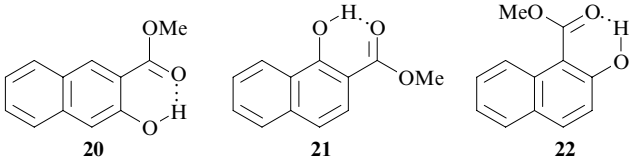
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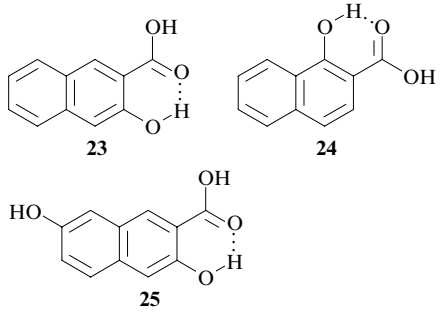
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Among *o*-hydroxynaphthoates in the ground state containing a hydrogen bond, namely, methyl 3-hydroxy-

2-naphthoate (**20**), methyl 1-hydroxy-2-naphthoate (**21**) and methyl 2-hydroxy-1-naphthoate (**22**), ESIPT was observed only in the first-mentioned compound.[54] The researchers believe [54] that high photostability of the studied compounds they found and the photostability of methyl salicylate are not related to the formation of a tautomer upon ESIPT. This conclusion was based on the fact that the photostability of compounds **21** and **22** in the molecules of which no excited state proton transfer takes place is comparable with the photostability of compound **2** (the efficiency ESIPT for this compound is 95%) and high photostability of compound **20** (5 times higher than that of compound **2**) is combined with low efficiency of ESIPT (according to the authors' estimate, only 1.8%).

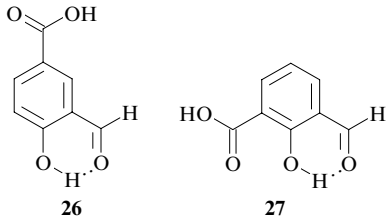


The long-wavelength band in the fluorescence spectrum of a solution of 3-hydroxy-2-naphthoic acid (**23**) is due to the emission of the ESIPT product.[55] Its relative intensity depends on the fluorophore concentration, the solvent nature, pH, the temperature and the excitation wavelength. The fluorescence characteristics of compound **23** in the polymer matrix depend on the concentration, the nature of the microenvironment and the excitation wavelength.[56] Two-band fluorescence of acid **23** is observed in aprotic polymers and one-band fluorescence with anomalous Stokes shift is observed in protic polymers. Conversely, the fluorescence spectrum of 1-hydroxy-2-naphthoic acid (**24**) has one band with a normal Stokes shift both in protic and aprotic polymers, which attests to the absence of ESIPT in this compound.

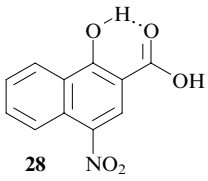


In aprotic solvents, the 3,7-dihydroxy-2-naphthoic acid (**25**) molecule does not undergo excited state proton transfer; in the authors' opinion,[57] this is caused by formation of dimers. In protic solvents, the occurrence of ESIPT in the presence of bases was demonstrated.

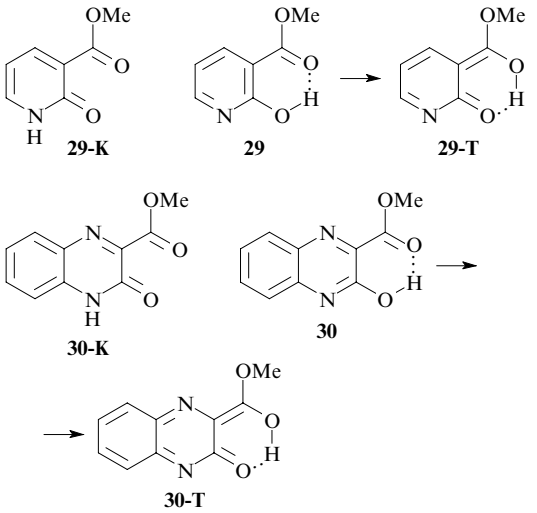
Upon excitation of 3-formyl-4-hydroxybenzoic acid (**26**), ESIPT occurs in aprotic solvents both at room temperature and at 77 K irrespective of the presence of the base.[58] As opposed to this, in the case of 3-formyl-2-hydroxybenzoic acid (**27**), ESIPT occurs only in aprotic solvents without addition of a base.[59]



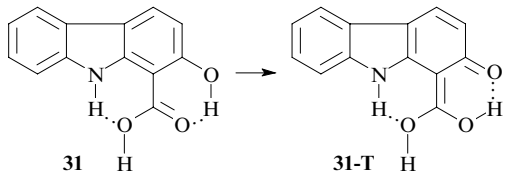
No excited state intramolecular proton transfer takes place in 1-hydroxy-2-naphthoic acid, but the introduction of a nitro group into the acid molecule gives rise to ESIPT in 1-hydroxy-4-nitro-2-naphthoic acid (**28**).[60] According to the authors,[60] this opens up a way to controlled ESIPT.



The excited state intramolecular proton transfer was found in methyl 2-hydroxynicotinate (**29**) (Ref. 61) and methyl 3-hydroxyquinoxaline-2-carboxylate (**30**).[62] According to the authors,[61, 62] in low-polar solvents, molecules **29** and **30** exist in the ground state as the enol form, while in polar solvents, they exist as the keto form (**29-K**, **30-K**). However, for compound **30** this conclusion contradicts the experimental absorption spectra, which are almost identical in non-polar and polar solvents. In the fluorescence spectra of compounds **29** and **30** in non-polar solvents, the band with anomalous Stokes shift was assigned to emission of the tautomers (**29-T**, **30-T**, respectively) formed upon the ESIPT.

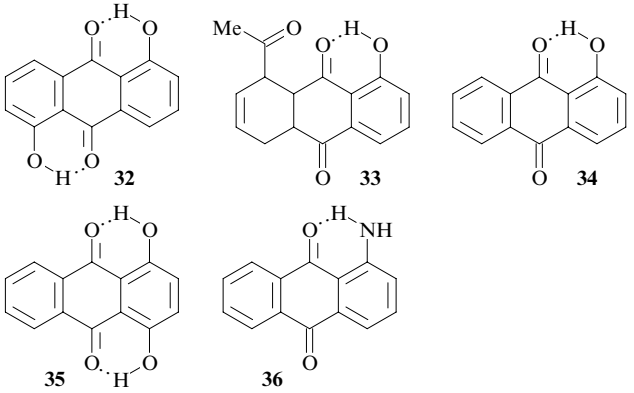


The two-band fluorescence following the excitation of the 2-hydroxy-9*H*-carbazole-1-carboxylic acid (**31**) molecule was attributed to the ESIPT to give the excited tautomer **31-T**.[63] The excited state intramolecular proton transfer occurs in all of the studied solvents except for cyclohexane (in which fluorophore is barely soluble) and water (intermolecular deprotonation in the ground state takes place).



31 **31-T**

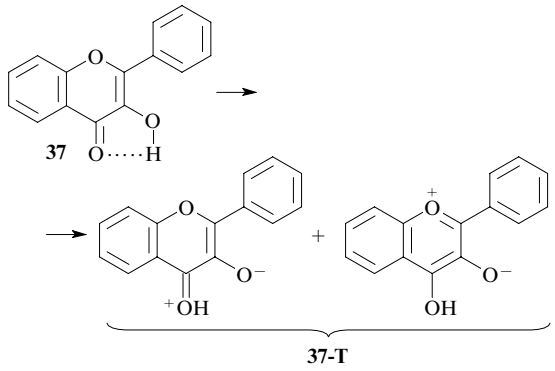
The excited state intramolecular proton transfer was found for 1,5-dihydroxyanthraquinone (**32**),[64] 1-acetyl-8-hydroxy-1,4,4*a*,9*a*-tetrahydroanthraquinone (**33**)[65] and 1-hydroxyanthraquinone (**34**),[66] but not for 1,4-dihydroxyanthraquinone (**35**)[64] or 1-aminoanthraquinone (**36**).[66]



32 **33** **34** **35** **36**

b. Hydroxyflavones

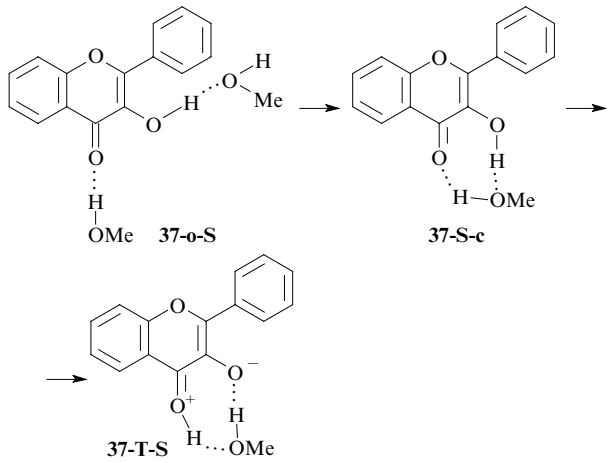
In a study of the spectral properties of 3-hydroxyflavone (**37**), Frolov *et al.*[67] observed two intense bands in the fluorescence spectrum in ethanol at 77 K. The authors assigned these bands to the emission of intermolecular and hydrogen-bonded intramolecular complexes. Sengupta and Kasha[68] interpreted these two fluorescence bands considering the excited state intramolecular proton transfer.



37 **37-T**

The long-wavelength band was assigned to the fluorescence of the excited tautomer **37-T**, which has formed upon the ESIPT, while the short-wavelength band was attributed to the fluorescence of a compound that has not undergone proton transfer. In view of the identity of the excitation spectra of the short-wavelength and long-wavelength fluorescence bands and the fact that substitution of deuterium for protium results in relative decrease in the intensity of the long-wavelength fluorescence band, it was proposed that the ESIPT does have a barrier.

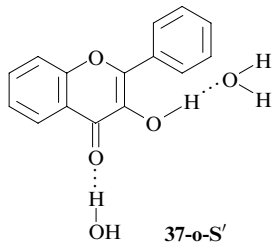
A study of the solvent effect on the excited state proton transfer in the 3-hydroxyflavone molecule showed[69] that in a hydrocarbon solvent, only closed conformer **37** exists in the ground state, while in a protic solvent, open conformer **37-o-S** exists. According to the authors, two different ESIPT mechanisms are possible: direct mechanism (in a hydrocarbon solvent, cyclohexane) and a mechanism involving a protic solvent (methanol) to give intermediate conformer **37-S-c**. The existence of a short-wavelength band in the fluorescence spectra of compound **37** in alcohols even at room temperature and in hydrocarbons at reduced temperature was attributed to the presence of a barrier to the ESIPT.



37-o-S **37-S-c** **37-T-S**

The short-wavelength fluorescence band of compound **37** is due to the emission of a species in which no ESIPT takes place due to high potential barrier. In a solution of poly(methyl methacrylate), the existence of more than one conformer of this compound in the ground state was assumed,[69] and this considerably complicates interpretation of the fluorescence observed for this system. Using the measurements of the fluorescence spectra and fluorescence kinetics of compound **37** in tetrahydrofuran, the activation energy of the ESIPT was determined (12 kJ mol^{-1}).[70]

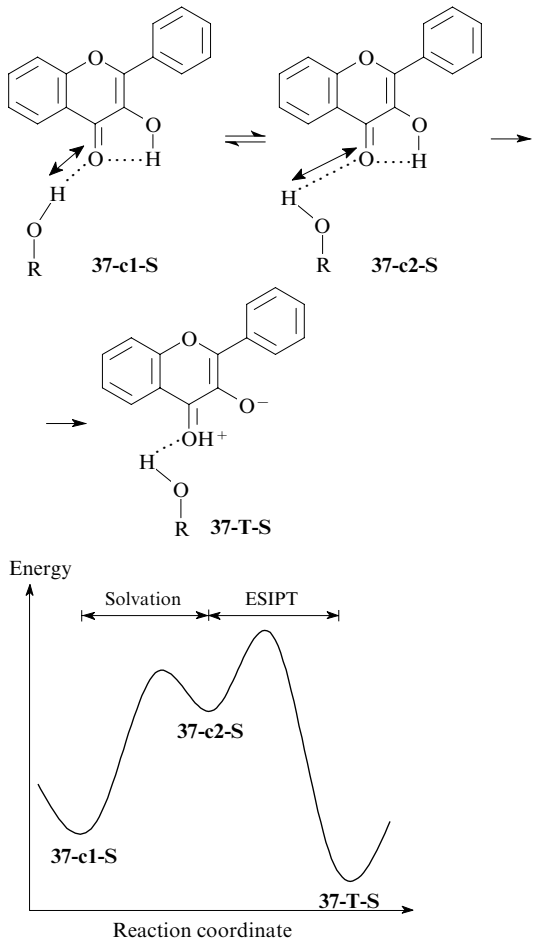
New results were obtained by using thoroughly dried hydrocarbon solvents: the short-wavelength fluorescence band of compound **37** was missing even at 77 K. This attests to almost barrierless direct (without a solvent) ESIPT.[71,72] The existence of a short-wavelength fluorescence band in the presence of water traces is due to emission of the polyhydrate form of compound (**37-o-S′**).



37-o-S′

In alcohol solutions, slow proton transfer in molecule **37** is related to the proton-donor properties of the solvent (Scheme 1).[73] The rate constant for the proton transfer is much lower in 2,2,2-trifluoroethanol and 2-chloroethanol than in methanol or ethanol, which have lower proton donor ability. This attests to an increase in the activation energy of the ESIPT with an increase in the ability of the solvent for hydrogen bonding. The activation energies of ESIPT in ethanol and 2-chloroethanol are 7 and 25 kJ mol^{-1}, respectively.

Scheme 1

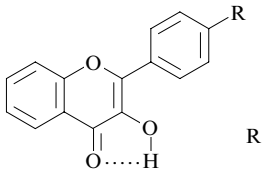


Study of the fluorescence kinetics of compound **37** in solid argon at 15 K showed that the building-up time of the long-wavelength band coincides with the time resolution of the instrument.[74] From this, it was concluded that the rate constant for the ESIPT is higher than 10^{12} s^{-1}, the potential barrier to the ESIPT is absent, and the reaction occurs during the excited state relaxation time.

With the advent of femtosecond absorption spectroscopy, there appeared the possibility to determine the ESIPT rates more accurately. In hydrocarbon solvents and in acetonitrile, the time of proton transfer in molecule **37** is 35 fs, while in ethanol, it is 60 fs. This was attributed[75] to stronger interaction of the fluorophore with the solvent. The researchers note that accurate determination of the proton transfer time is restricted by instrumental possibilities and in reality it can be even shorter. In ethanol solutions, the ESIPT kinetics was found to have a picosecond component, which was assigned to the excited state proton transfer to the solvent molecule.

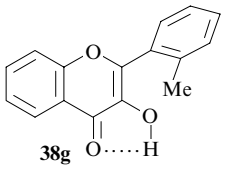
The times of the ESIPT and the back proton transfer in the ground state of compound **37** in octane are 39 and 210 fs, respectively.[76] Upon the replacement of the hydroxy proton in **37** by deuteron, the rate constant for the ESIPT decreases 4-fold, which is indicative of the tunnelling mechanism of this process.

The introduction of electron-donating substituents into molecule **37** results in electron density redistribution and affects considerably the rates of the ESIPT and the back proton transfer in the ground state. For 3-hydroxyflavone derivatives, namely, 3-hydroxy-2-(4-methylphenyl)chromen-4-one (**38a**), 3-hydroxy-3-(4-methoxyphenyl)chromen-4-one (**38b**), 3-hydroxy-2-(4-chlorophenyl)chromen-4-one (**38c**) and 3-hydroxy-2-(4-cyanophenyl)chromen-4-one (**38d**), the measured ESIPT time was less than 200 fs.[75]

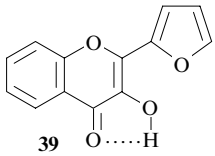


38a–e

R = Me (**a**), OMe (**b**), Cl (**c**), CN (**d**), NMe_2 (**e**).



38g



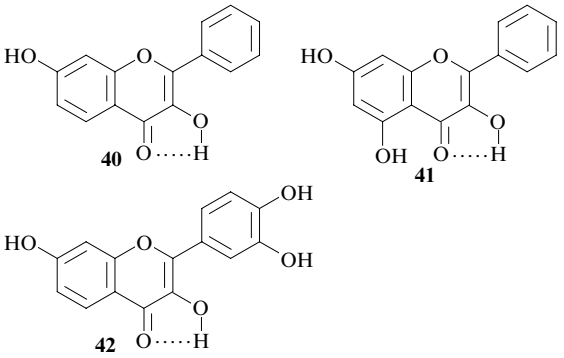
39

The ESIPT times in 3-hydroxyflavone, 3-hydroxy-2-(4-methoxyphenyl)chromen-4-one and 3-hydroxy-2-furylchromen-4-one (**39**) determined by spectroscopy of polyatomic molecules by the Shpolskii method in the n-octane matrix are 93, 210 and >600 fs, respectively. The back proton transfer times for these compounds are 210, 470 fs and >2 ps, respectively.[77]

The introduction of the methyl group in the *ortho*-position of the phenyl group results in mutual twisting of the two aromatic fragments in **38g** and in an increase in the negative charge on the hydroxyl oxygen and the positive charge on the carbonyl oxygen.[78] This weakens the intramolecular hydrogen bond and increases the activation energy of the ESIPT.

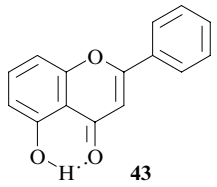
The relationship between the intramolecular processes of charge and proton transfer upon femtosecond excitation of 3-hydroxy-2-(4-dimethylaminophenyl)chromen-4-one (**38e**) was established. In the opinion of researchers cited,[78] no charge transfer takes place in non-polar solvents upon excitation of a non-planar fluorophore structure but abnormally slow ESIPT (2 ps) takes place. In polar solvents, charge transfer is fast (100–200 fs), and after the resulting structure has stabilized, slow ESIPT takes place (over several tens of picoseconds).[79]

As pressure increases in the range of 10–30 kbar, the formation of the ESIPT tautomer in solutions of 3-hydroxyflavone in isobutyl alcohol and glycerol[80] and in polymer matrices, *viz*., poly(methyl methacrylate), poly(vinyl acetate), polyacrylic acid and cellulose acetate,[81] is suppressed, and this leads to enhanced fluorescence of the initial species. According to the authors,[81] this effect is caused by the shift of the **37*** ⇄ **37-T*** equilibrium in the excited state. Similar results were obtained for polyhydroxyflavones, 3,7-dihydroxyflavone (**40**), 3,5,7-trihydroxyflavone (**41**) and 3,7-dihydroxy-2-(3,4-dihydroxyphenyl)chromen-4-one (**42**), in the above-listed polymer matrices[82] and for solutions of 3-hydroxy-2-(4-dimethylaminophenyl)chromen-4-one (**38e**) in polyacrylic acid, cellulose acetate, polyacrylonitrile, poly(methyl methacrylate) and poly(vinyl chloride).[83] The pressure increase inhibits the ESIPT in all of the polymers studied.



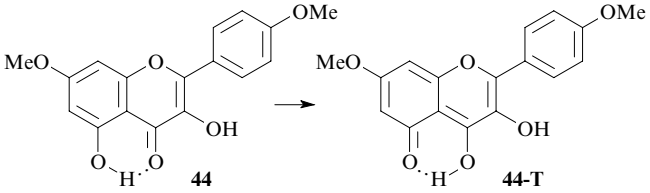
The exited state proton transfer in molecule **37** takes place not only in the condensed phase but also in the vapour.[84] The fluorescence quantum yield of the tautomer depends in this case on the excitation energy, and this may indicate that the proton transfer takes place at higher vibrational sublevels of the electronically excited state S_1.

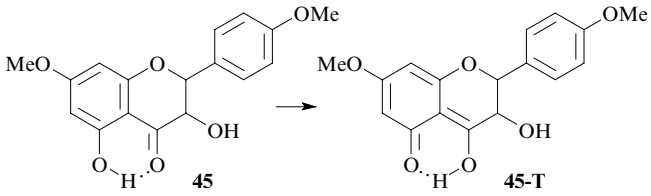
The fluorescence spectrum of 5-hydroxy-2-phenylchromen-4-one (**43**) in cyclohexane exhibits two bands with maxima at 420 and 700 nm.[85] The short-wavelength band refers to the initial form of compound **43** and the long-wavelength band corresponds to the tautomer formed upon ESIPT over a period of < 160 fs. The time resolution of the instruments did not allow one to reveal changes in the ESIPT rate following replacement of protium by deuterium.



The proton transfer from the hydroxy group to 3-hydroxyflavone in the ground electronic state to the alcohol molecule in neutral alcohol solutions was reported.[86] However, in view of the rather low basicity of the alcohol and acidity of compound **37** in the ground state, this reaction seems unlikely. In most studies, the absorption band that was assigned to the anion was not observed for alcohol solutions.[69, 73, 78] The presented proof for the occurrence of this reaction gives rise to doubt. Note that purification of alcohols by calcium hydride may leave traces of the base; therefore, the anionic form of the fluorophore in the ground state may appear.

The fluorescence spectra of 3,5-dihydroxy-7-methoxy-2-(4-methoxyphenyl)chromen-4-one (**44**) and 3,5-dihydroxy-7-methoxy-2-(4-methoxyphenyl)chroman-4-one (**45**) in hydrocarbon solvents were found to exhibit three bands.[87] Two bands in the UV region with maxima at 290 and 340 nm were assigned to emission localized on anisole and benzopyrone rings, respectively; the third long-wavelength band with a maximum at 550 nm was attributed to the emission of the ESIPT product (**44-T**, **45-T**).



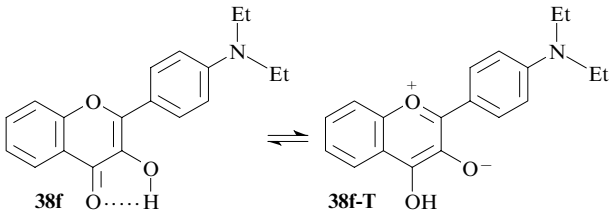


Encapsulation of compounds **37** and **42** in chemically modified β-cyclodextrin enhances the fluorescence of the ESIPT tautomer.[88] According to the authors, both flavonols occur in the hydrophobic environment where the intermolecular hydrogen bonds and polar relaxation effects are minimized.

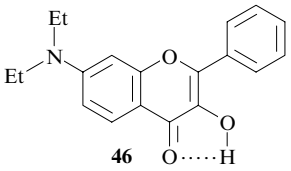
The photophysical characteristics of 3-hydroxyflavone **37** in aqueous micellar solutions attest to the presence of ESIPT and the independent intermolecular proton transfer in the ground state.[89] The latter process accounts for the absorption in the long-wavelength region and appearance of the corresponding fluorescence. The intramolecular proton transfer gives rise to two-band fluorescence: the short-wavelength band corresponds to the excitation of the initial molecule and the long-wavelength band corresponds to the ESIPT product, *viz*., excited tautomer. The ESIPT dynamics in aqueous micellar solutions is similar to the ESIPT dynamics in protic solvents.

A study of the photophysical behaviour of the ESIPT tautomer and the anion in the ground state of 3-hydroxyflavone in the liposomal membrane showed that the fluorescence of the ESIPT tautomer is emitted from the portion of the fluorophore that is located inside the hydrophobic shell and the fluorescence of the anion in the ground state is emitted from the portion of the fluorophore that is located near the water surface. The ratio of these fluorophore portions changes with temperature, in particular, the fraction of the anion increases.[90]

Upon excitation of 3-hydroxy-2-(4-diethylaminophenyl)chromen-4-one (**38f**) in polar solvents, the fast charge transfer is followed by relatively slow (over a period of several hundreds of femtoseconds) ESIPT, which competes with the solvent relaxation.[91] Different equilibrium polarizations of molecules **38f** and **38f-T** give rise to solvent-induced barrier to the ESIPT. It was suggested[91] that ESIPT in compound **38f** is an equilibrium process.



The excited state intramolecular proton transfer in 3-hydroxy-2-phenyl-7-diethylaminochromen-4-one (**46**) in polar media competes with the solvent relaxation caused by fast charge transfer ($\leqslant 120$ fs).[92] The solvent-induced barrier to the ESIPT is 15 kJ mol^{-1}. The researchers believe[91] that the excited state proton transfer in molecule **46**, unlike that in 3-hydroxyflavone derivative **38f**, is an exoergic process, and, hence, it is irreversible.

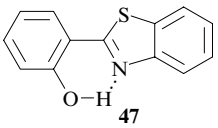


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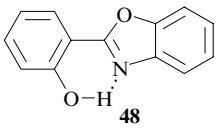
A time-of-flight fluorescence spectroscopy study of the excited state proton transfer in molecule **38f** in ionic liquids based on the imidazolium ion showed that the maximum of the short-wavelength fluorescence spectrum gradually shifts to longer wavelengths in the subnanosecond time range, and the emission of the fluorescence of the ESIPT tautomer is delayed relative to the short-wavelength fluorescence.[93] These results are indicative of the considerable role of the solvation processes taking place immediately after excitation in the ESIPT mechanism.

2. Complexes with the O−H···N≤ bond

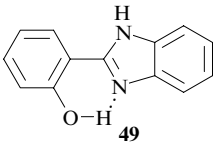
Yet another type of strong hydrogen bond is the O−H···N≤ bond. The fluorescence spectra of compounds with such hydrogen bond typically exhibit a long-wavelength band with anomalous Stokes shift. This band is caused by emission of the tautomer formed upon ESIPT. 2-(2-Hydroxyphenyl)benzazoles, namely, 2-(2-hydroxyphenyl)benzothiazole (**47**), 2-(2-hydroxyphenyl)benzoxazole (**48**) and 2-(2-hydroxyphenyl)benzimidazole (**49**), are the best studied compounds with this type of intramolecular hydrogen bond.



47



48



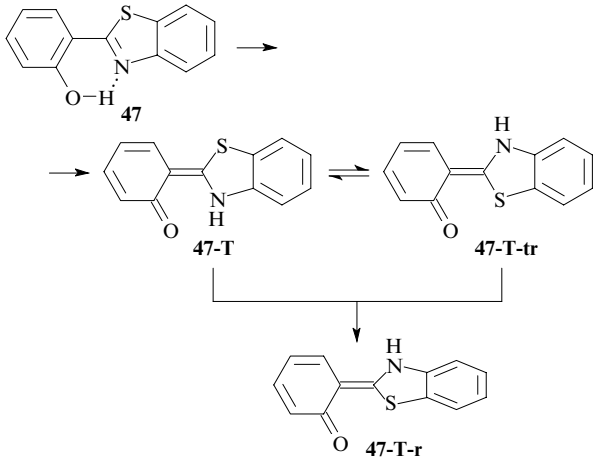
49

a. Hydroxy(benzo)thiazoles

The intramolecular proton transfer in hydroxy(benzo)thiazoles is the subject of numerous publications.[94–131] The data on temporal characteristics of the ESIPT are being corrected with the advent of investigation methods for fast reactions. The first femtosecond study of the excited state proton transfer in the 2-(2-hydroxyphenyl)benzothiazole molecule was carried out by Elsaesser and co-workers.[107] After a 140 fs excitation pulse, the measured time of ESIPT in a solution of 2-(2-hydroxyphenyl)benzothiazole in tetrachloroethylene at 293 K was 170 fs. The same time was observed for deuterated compounds, which confirms the absence of a barrier to the ESIPT.[108]

Using a 30 fs excitation pulse, Lochbrunner *et al.*[123] found that the excited state proton transfer of molecule **47** in cyclohexane occurs within 60 fs. The electronic configuration changes over the same period of time; the ESIPT induces coherent vibrations along four skeletal modes. The hydrogen bonded ring is contracted during and after the proton transfer.

The ESIPT takes place in the fragment with intramolecular hydrogen bond between the hydroxy group and the nitrogen atom, resulting in the neutral or zwitter-ion form of tautomer **47**. The zwitter-ion structure was postulated for tautomer **47** in the crystal.[95] Meanwhile, in picosecond IR spectroscopy studies of the ESIPT product in solution, bands at 1540 and 3000 cm^{-1} coinciding with C=O and NH vibrations of the keto form were found.[109] The ESIPT product, *cis*-keto form (**47-T**), can undergo rotational isomerization to give *trans*-keto form (**47-T-tr**).



The *cis* (**47-T**) and *trans* (**47-T-tr**) forms of the intermediate tautomer in the ground electronic state with lifetimes in the microsecond range were detected.[112–114, 117, 124] One more species, rotated intermediate product (**47-T-r**) between the *cis* and *trans* structures, was proposed to interpret the effective radiationless deactivation of tautomer **47-T**.[106, 112] The irradiation of compound **47** in polystyrene gives rise to new absorption and emission bands, which disappear after heating the sample to 90 °C. The new bands were assigned to *trans*-keto-conformers in the ground state, which are formed from the *trans*-keto forms in the excited state.[125] This may occur if the barrier to the *cis*–*trans* rotation in the excited state is much lower than this barrier in the ground state.

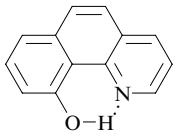
In a study of the excited state proton transfer in molecule **47** in tetrachloroethylene by femtosecond time-of-flight IR spectroscopy, a 30–50 fs delay of the appearance of the C=O longitudinal vibrations was observed.[126] According to the authors, this means that the ESIPT occurs within 30–50 fs. The centre of the C=O absorption band in the keto tautomer shifts by 3–5 cm^{-1}. This effect is caused by the intramolecular redistribution and vibrational energy relaxation.

Fast vibrationalal relaxation processes were detected by measuring intermediate vibrational spectra of excited molecules **47**. The vibrational bands of the keto form were found to shift to shorter wavelengths to 7 cm^{-1} in the S_1 state. The fast component of this shift was assigned to the intramolecular redistribution of the excess vibrational energy, which is followed by slow picosecond transfer of excess energy to the solvent.[127]

The detailed mechanism of the excited-state proton transfer in molecule **47** in cyclohexane was studied by femtosecond time-resolved absorption spectroscopy at 30 fs. After 33 fs from excitation, the molecule acquires the keto configuration and 20 fs later, it approaches the potential minimum of the keto form. The time of transfer is

related to the inertia of movement of the molecular skeleton rather than to the probability of tunnelling or proton transfer over the barrier. The ESIPT dynamics is determined by the evolution of the wave packet along several coordinates of the molecular skeleton.[128] The participation of skeletal deformations in the ESIPT was confirmed by quantum chemical calculations.[129] The vibrational modes active in this process were identified.

For compound **47** and 10-hydroxybenzo[*h*]quinoline (**50**), it was shown that the ESIPT occurs over periods of 30–40 fs as a result of skeletal deformations rather than simple migration of the hydrogen atom. In both systems, skeletal deformations result in shortening of the O–N distances in such a way that the hydrogen atom can form a new bond with nitrogen without a barrier. In the case of compound **47**, skeletal deformations are the key modes for proton transfer. Conversely, in the case of compound **50**, the mode of hydrogen atom migration is only activated by the skeletal deformation modes, and stretching of the O–H bond plays a more active role.[130]



50

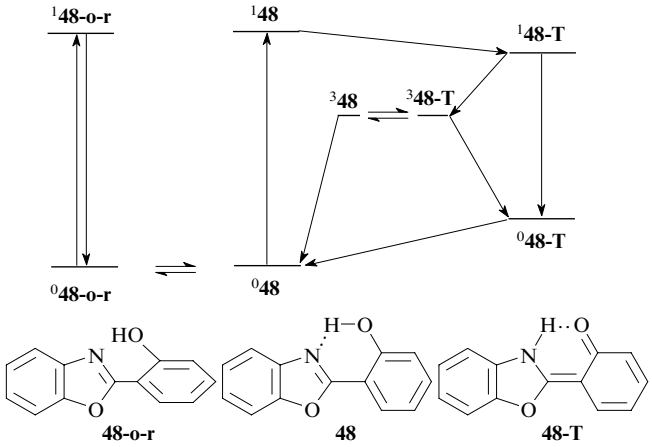
The dynamics of excited state proton transfer in molecules **47** and **48** have much in common according to the femtosecond absorption spectroscopy data. After optical excitation by a 30 fs pulse, the wave packet formed propagates along the adiabatic potential surface of the state S_1. The propagation of the wave packet is related to bending of the molecular skeleton, which reduces the distance between the proton donor and acceptor. The change in the electronic configuration occurs after sufficient compression of the molecule and results in the formation of bonds in the ESIPT product. The shape of the potential energy surface is determined by the interaction between the electronic configurations of the enol and the keto form, and the formation of new bonds can be described as mixing of both configurations upon wave packet propagation.[131]

b. Hydroxy(benz)oxazoles

The excited state proton transfer in hydroxy(benz)oxazole molecules is the subject of a number of publications.[95,117–122,132–173] The fluorescence spectra of 2-(2-hydroxyphenyl)benzoxazole in hydrocarbon solvents show two bands: a short-wavelength and a long-wavelength band with anomalous Stokes shift.[117,133] The long-wavelength band is caused by emission of the tautomer, the ESIPT product, while the short-wavelength band is due to the emission of species where no ESIPT took place. Woolfe *et al.*[133] was the first to explain this by existence of equilibrium between the species with the O–H···N$\leqslant$ intramolecular hydrogen bond (**48**) and the species with no such bond (**48-o-r**) in the ground state (Scheme 2). This assumption is confirmed experimentally by the difference between the excitation spectra of two fluorescence bands.

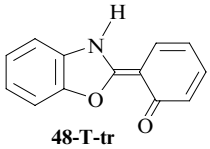
A decrease in the intensity of the long-wavelength band and increase in the intensity of the short-wavelength band

Scheme 2



were found in a study of the fluorescence of 2-(2-hydroxyphenyl)benzoxazole in polymer matrices at pressures from 10 to 60 kbar. This change in the band intensity was attributed to the shift of the equilibrium in the ground state between the species with the intramolecular hydrogen bond (**48**) and that without such bond (**48-o-r**).[151]

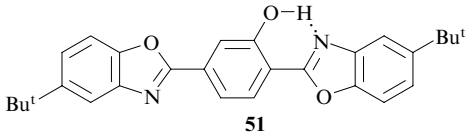
The product of the excited state proton transfer in molecule **48**, namely, *cis*-keto tautomer **48-T**, is transformed, similarly to other 2-hydroxyphenylbenzazoles, to *trans*-keto tautomer (**48-T-tr**) as a result of internal rotation.[141]



48-T-tr

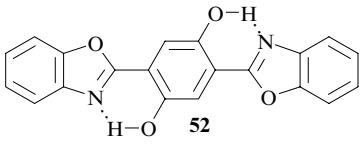
The quantum yield of **48-T-tr** depends on the temperature and becomes negligibly low below 160 K. In dry inert solvents, tautomer **48-T-tr** undergoes double proton transfer by a bimolecular mechanism to be slowly converted to the enol form. Water traces substantially accelerate the back proton transfer to give the enol.

For solutions of 2,5-bis(5-*tert*-butylbenzoxazol-2-yl)-phenol (**51**) in hexane, fluorescence of the enol and keto tautomers was observed.[153] The excitation spectra and the fluorescence lifetimes of both forms are equal. In a cold supersonic jet flow, fluorescence of only keto tautomer is observed. The OH/OD isotope effect is absent in this case, indicating a low energy barrier to the ESIPT.

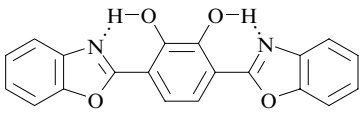


51

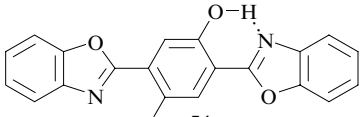
The excited state proton transfer is also observed in 'double' benzoxazoles, 2,5-bis(benzoxazol-2-yl)hydroquinone (**52**) and 3,6-bis(benzoxazol-2-yl)catechol (**53**).[154–167] The type of ESIPT (single or double) was elucidated using monomethoxy derivatives, 2,5-bis(benzoxazol-2-yl)-4-methoxyphenol (**54**) and 3,6-bis(benzoxazol-2-yl)-2-methoxyphenol (**55**).



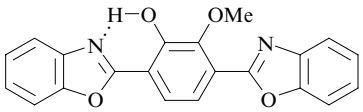
52



53



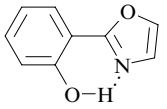
54



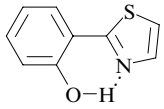
55

In the singlet excited molecule **52**, the transfer of only one proton takes place with overcoming a potential barrier.[155] In the authors' opinion, an equilibrium is rapidly established between the initial species and the ESIPT tautomer, the ESIPT process being completely reversible. First, it was considered that the ESIPT tautomer of compound **53** is the product of a barrierless transfer of two protons. The potential barrier to the ESIPT for compound **52** is 121 cm^{-1} (Ref. 156). The authors' conclusion about the tunnelling mechanism of the ESIPT was confirmed by the fact that on replacement of the proton by deuteron, the relative intensity of the ESIPT tautomer emission decreases twofold.[157] The existence of a barrier and the tunnelling mechanism of ESIPT were confirmed by measurement of the benzoxazole **52** fluorescence in non-polar solvents at low temperature.[158] The rate constants for the forward and reverse ESIPT for compounds **52**–**54** in non-polar solvents are $\sim 10^{10}$ s^{-1}, which is much lower than the values typical of reactions of this class.[159] The relatively low rate constant for the ESIPT of benzoxazole **53** does not agree with the earlier assumption about the barrierless nature of this process.[154, 155] The reversibility of the ESIPT in compounds **52**,[160, 161] **54**[160] and **53**[161] was confirmed by studies of the fluorescence kinetics. On the basis of analysis of the temperature dependence of the buildup time of the ESIPT tautomer fluorescence, it was concluded that the transfer in benzoxazole **52**–**54** molecules is accompanied by overcoming an energy barrier, and this accounts for low rate constants for the ESIPT.[162] The rate constant for the ESIPT of compound **52** in solid argon at 15 K exceeds 8×10^{10} s^{-1}. This value attests to the absence of a potential barrier to the ESIPT or to the tunnelling mechanism of this process at low temperature.[163, 164] The discovered short-wavelength fluorescence with normal Stokes shift was attributed to the emission of dimer **52**. On the basis of comparison of the photophysical characteristics of compounds **53** and **55** and semiempirical quantum chemical calculations, the ESIPT mechanism in compound **53** was refined:[167] unlike the previously proposed two-proton mechanism of the ESIPT, the researchers cited[167] arrived to the conclusion that in molecule **53**, as in compound **52**, transfer of only one proton takes place to give monoketo tautomer.

2-(2-Hydroxyphenyl)oxazole (**56**) and 2-(2-hydroxyphenyl)thiazole (**57**) are similar to their benzo analogues **48** and **47**. These compounds tend to exhibit two-band fluorescence in polar and protic solvents due to the existence of several conformers in the ground state. This is supported by the presence of short-wavelength and long-wavelength fluorescence bands in the excitation spectra.[168] In the excited tautomer with the transferred proton, the barrier to the rotation decreases, which results in a twisted biradical structure. This facilitates deactivation to the triplet state.

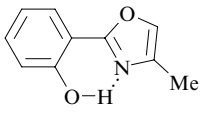


56



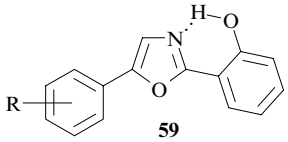
57

It was shown by calculations that the excited state proton transfer in the 2-(2-hydroxyphenyl)-4-methyloxazole (**58**) molecule in the gas phase and in β-cyclodextrin do not differ much. The energy barrier to the ESIPT is rather low. However, the energy barrier to the internal rotation in the keto form is much higher. Femtosecond studies showed that the fast ESIPT is followed by slow internal rotation process.[169, 170]

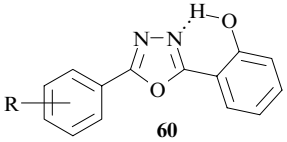


58

The excited state proton transfer in the 5-aryl-2-(2-hydroxyphenyl)oxazole (**59**) and 5-aryl-2-(2-hydroxyphenyl)-1,3,4-oxadiazole (**60**) molecules is accompanied by considerable radiationless deactivation of the tautomer.[171]



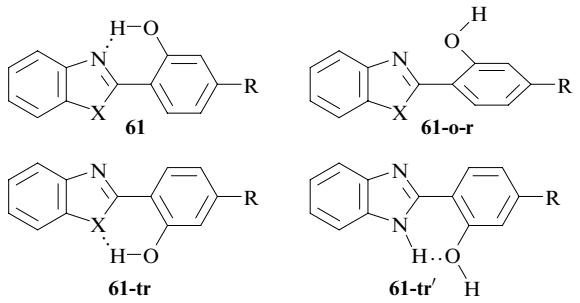
59



60

The efficiency of the tautomer fluorescence markedly increases upon the introduction of electron-withdrawing substituents into both the proton-acceptor and the proton-donor fragments.

New fluorescent benzazolylphenylene monomers and polymers **61** with ESIPT were proposed.[172] The benzoxazole and benzimidazole derivatives fluoresce in the blue spectral region and benzothiazole derivatives fluoresce in the green region of the spectrum. The two-band fluorescence observed in some solutions is attributable to the existence of the conformational equilibrium in the ground state depending on the solvent polarity. The short-wavelength band belongs to rotamers **61-o-r**, **61-tr**, **61-tr′** in the molecules of which no proton transfer takes place, and the long-wavelength band corresponds to the excited state proton transfer in the molecule of rotamer **61**.



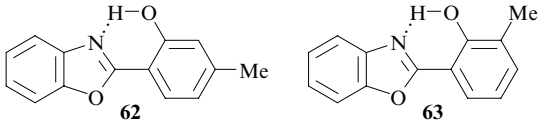
X = O, S, NH.

The excited state proton transfer in molecule **48** occurs also in the triplet state.[135–140, 142, 143] The triplet states ^{3}**48-T** and ^{3}**48** are populated only from the S_1 state of the keto form resulting from the ESIPT.[135] The back proton transfer in the triplet state ^{3}**48-T** → ^{3}**48** is an important low-temperature deactivation path.

Molecule **48** emits double phosphorescence caused by the enol form and the keto form.[136, 137] The relationship of the bands almost does not depend on temperature. Both phosphorescence bands of solutions of compound **48** in liquid hydrocarbons decay monoexponentially with equal rate constants;[136] the kinetics of phosphorescence decay of frozen glassy solutions is polyexponential.[137]

The triplet sates of both tautomers (unlike the lower excited singlet state) are nearly isoenergetic and separated by a barrier of $\sim$30–50 kJ mol^{-1} (Ref. 138). For triplet molecule **48** in liquid non-polar solvents in the temperature range of 55–200 K, the keto–enol equilibrium is established. At low temperature, ESIPT follows a tunnelling mechanism.

In the molecules of benzoxazole **48** and 2-(2-hydroxy-4-methylphenyl)benzoxazole (**62**) and their deuterated analogues in the triplet state, the excited state proton transfer occurs by a tunnelling mechanism over a temperature range of 35–250 K in alkanes which markedly differ in viscosity at low temperature.[139, 140] In triplet compound **48**, the excited state transfer is reversible, because the two forms are isoenergetic, while for compound **62** this process is shifted towards the enol form as the keto form has a higher energy than the enol form. Despite this difference, the observed rate constants for the ESIPT of these two compounds have almost equal values. The temperature dependence of the rate constant for the ESIPT is insensitive to the solvent viscosity, *i.e.*, the proton tunnelling in these compounds does not depend on the molecular friction at intermediate or very low temperatures.



The enol triplet level of the 2-(2-hydroxy-3-methylphenyl)benzoxazole (**63**) molecule is located higher than in molecule **62**; therefore, no ESIPT takes place.[173]

c. Hydroxy(benzo)imidazoles

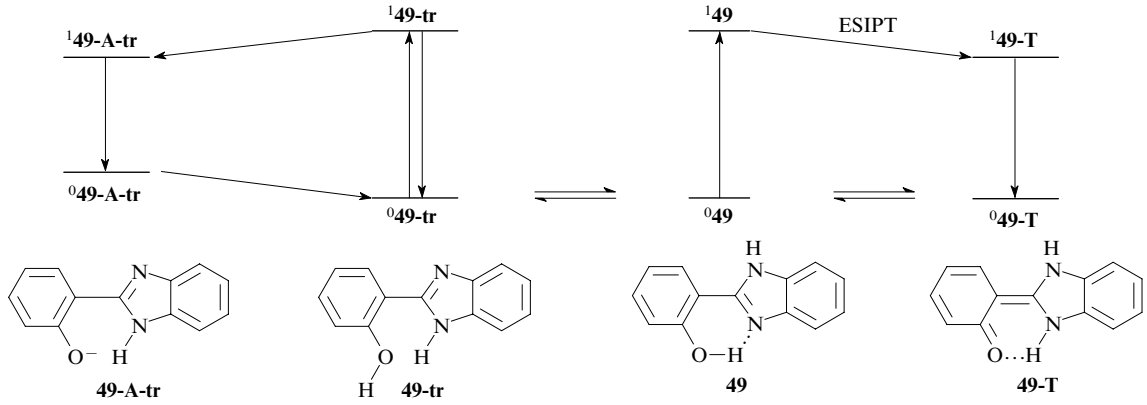
A number of publications[95, 152, 174–186] are devoted to the study of ESIPT in hydroxy(benz)imidazoles and -triazoles. There are two rotamers of 2-(2-hydroxyphenyl)benzimidazole (**49**) in the ground state occurring in equilibrium.[176] The excitation of one of them produces normal fluorescence, whereas the other rotamer undergoes ESIPT and forms the tautomer with large Stokes shift of the fluorescence. The existence of two rotamers is supported by different excitation spectra of the normal and tautomer fluorescence. Quantum chemical calculations showed that the barrier to the interconversion of the rotamers in the excited state is higher than in the ground state both for compound **49** and for benzothiazole **48**; therefore, the rotamer interconversion in the excited state is hampered.[152]

In neutral aqueous solutions, compound **49** exists in the ground state as three forms related by tautomeric and conformational equilibria.[175] In addition to *cis*- (**49**) and *trans*-enol (**49-tr**) forms, keto form (**49-T**) also exists (Scheme 3).

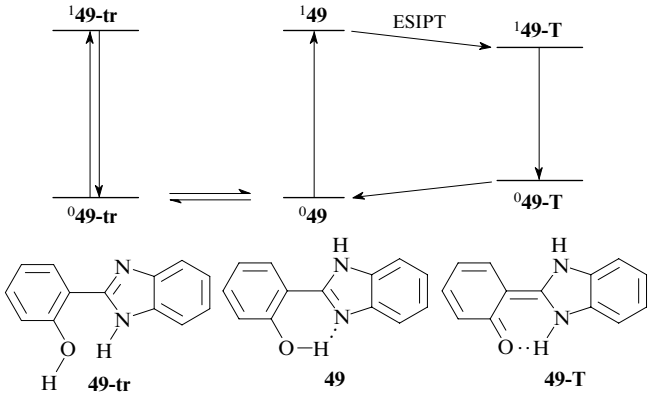
An ethanol solution contains only forms **49** and **49-tr**, which occur in conformational equilibrium (Scheme 4).

The *cis*-enol form undergoes the ESIPT both in water and in ethanol, resulting in the excited keto form (**49-T**), which fluoresces with anomalous Stokes shift. In both solvents, no excited state proton transfer takes place in **49-tr**. The emission of this form in ethanol accounts for the short-wavelength fluorescence. In water, excited state intermolecular proton transfer to the solvent molecule takes place to give the excited anion **49-A-tr** (see Scheme 3).

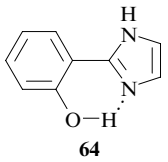
Scheme 3



Scheme 4



The fluorescence spectra of 2-(2-hydroxyphenyl)imidazole (**64**),

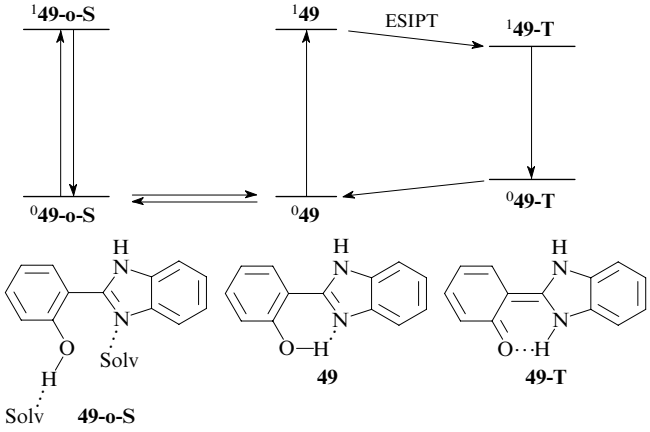


2-(2-hydroxyphenyl)benzimidazole and their derivatives in dry non-polar solvents exhibit only one band with abnormally large Stokes shift, which has been assigned to the tautomer formed upon the ESIPT.[179]

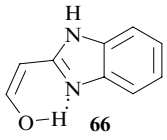
The appearance of short-wavelength fluorescence with normal Stokes shift in solutions of these fluorophores in proton-donor solvents was attributed to the presence of a minor fraction of the open enol form (**49-o-S**) in the ground state, which does not undergo excited state tautomerization (Scheme 5). This explanation differs from the model proposed by other authors.[152, 175, 176]

The ground-state 2-(2-hydroxyphenyl)-1-methylbenzimidazole (**65**) exists in a solvent-dependent conformational equilibrium (Scheme 6).[174] The *cis*-enol conformer (**65**) having an intramolecular hydrogen bond and a planar structure predominates in aprotic solvents; it undergoes the ESIPT to give the keto tautomer (^{1}65-T). In aqueous solution, only non-planar enol conformer (**65-o-r**) exists; on its excitation, proton transfer to a water molecule takes place to give an excited anion. In alcohol solutions, both enol conformers are present, the ratio between them being determined by the solvent acidity. The *cis*-enol conformer undergoes the ESIPT, while the non-enol conformer undergoes internal rotation to give a planar structure (**65-o**) devoid of the intramolecular hydrogen bond; this species emits fluorescence with a normal Stokes shift.

Scheme 5



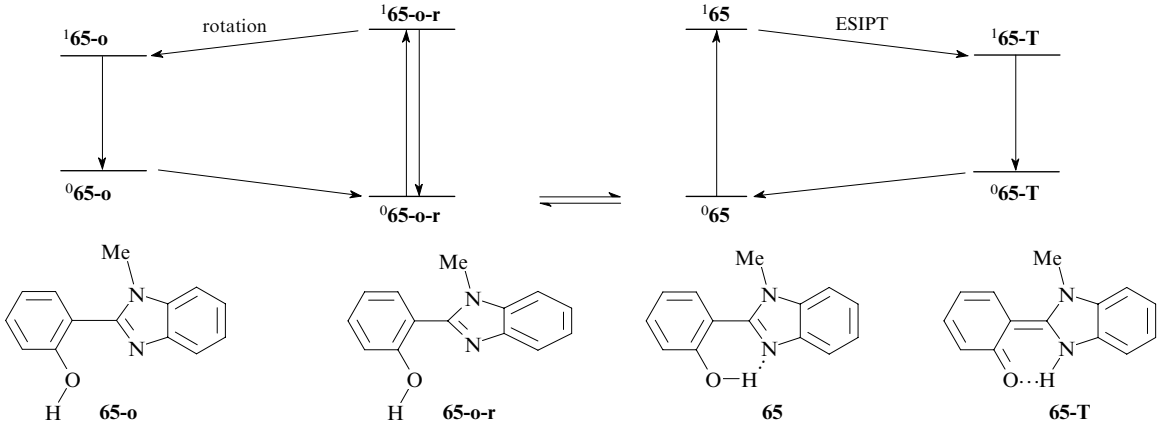
The existence of different rotamers in the ground state of 2-(2-hydroxyphenyl)imidazole (**64**) and 2-(2-hydroxyvinyl)benzimidazole (**66**) was confirmed by quantum chemical calculations.[180]

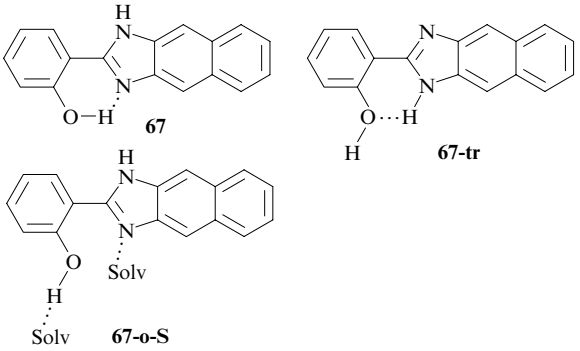


It was concluded[180] that the rotamerism in compound **64** in the ground and excited states is similar to that in 2-(2-hydroxyphenyl)benzimidazole (**49**) (see Refs 152, 175, 176). The enol *cis*- and *trans*-rotamers are interconverted in the ground state but not in the excited state. For 2-(2-hydroxyvinyl)benzimidazole, the interconversion is hampered in both the ground and excited states.

The presence of three different conformers in the ground state of 2-(2-hydroxyphenyl)-1*H*-naphtho[2,3-*d*]imidazole (**67**) was shown.[181] Rotamer **67-tr**, which emits normal fluorescence and does not undergo ESIPT, and rotamer **67**, which undergoes ESIPT upon excitation, exist in non-polar solvents.

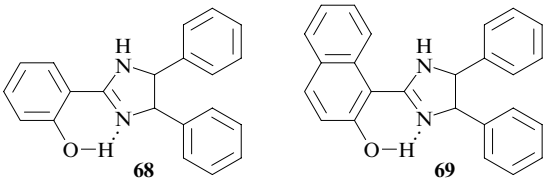
Scheme 6



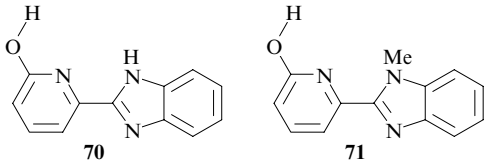


The ESIPT tautomer thus formed shows a fluorescence spectrum with abnormally large Stokes shift. In proton-donor solvents, open conformer **67-o-S** hydrogen-bonded to the solvent exists apart from the rotamers **67** and **67-tr**. The increase in the intensity of the short-wavelength fluorescence upon the addition of water or methanol to a fluorophore solution in dioxane is attributable to either increase, in the ground state, of the fraction of the rotamer in which the ESIPT is impossible or decrease of the rate of radiationless deactivation of this excited rotamer.

The time of the excited state proton transfer in the 2-(2-hydroxyphenyl)-4,5-diphenyl-2(1*H*)-imidazole (**68**) molecule having a planar structure of the reaction site is short (< 100 fs), while that in the 2-(2-hydroxy-1-naphthyl)-4,5-diphenyl-2(1*H*)-imidazole molecule (**69**) having a non-planar structure of the reaction site and, hence, weakened intramolecular hydrogen bond increases ~3.5-fold (since the ESIPT time is determined by the time of the conformational rearrangement of the molecule).[182, 183]

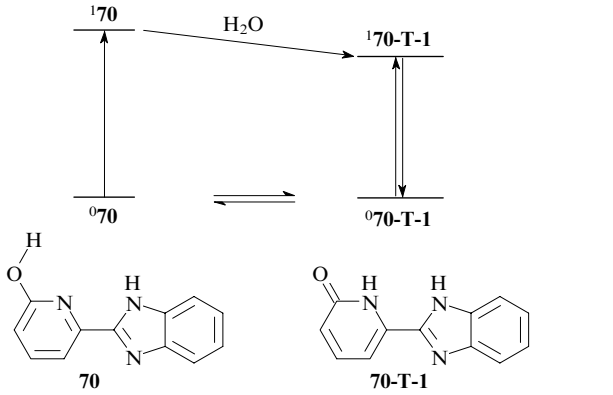


A tautomeric equilibrium depending on the solvent was found for 2-(6-hydroxy-2-pyridyl)benzimidazole (**70**) and 2-(6-hydroxy-2-pyridyl)-1-methylbenzimidazole (**71**) in the ground state between lactim (**70**) (normal form) and lactam (**70-T-1**) (tautomer) formed upon the proton transfer from the hydroxy group to the nitrogen atom of the pyridine ring.[184]



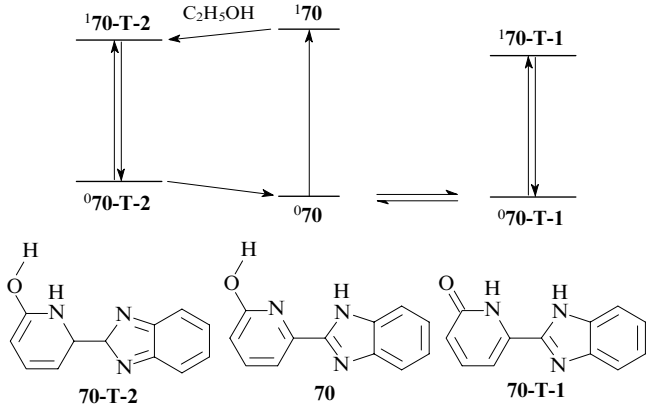
In acetonitrile (aprotic solvent), ESIPT is not observed. Protic solvents (ethanol and water) facilitate the excited state proton transfer but each solvent catalyzes a particular ESIPT process. In water, excited lactim molecules (**^{1}70**) undergo proton transfer from the hydroxy group to the pyridine nitrogen atom (OH→N transfer through a water molecule) to give lactam tautomer **^{1}70-T-1** (Scheme 7).

Scheme 7



In compound **^{1}70** dissolved in ethanol, proton transfer from the benzimidazole NH group to pyridine nitrogen takes place (NH→N transfer through the alcohol molecule) to give a new tautomer (**^{1}**70-T-2), which is absent in the ground state (Scheme 8).

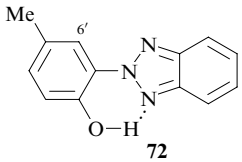
Scheme 8



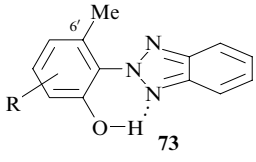
This reaction is not observed in 2-(6-hydroxy-2-pyridyl)-1-methylbenzimidazole devoid of the NH group.

d. 2-(2-Hydroxyphenyl)benzotriazoles

The excitation of 2-(2-hydroxy-5-methylphenyl)benzotriazole [Tinuvin-P (**72**)] induces fast ESIPT with a rate constant of 10^{13} s^{-1}. The tautomer passes to the ground state at a rate constant of 6.7×10^{12} s^{-1} and the back proton transfer in the ground state is characterized by a rate constant of 1.7×10^{12} s^{-1} (Ref. 185).

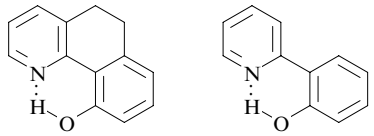


The introduction of a methyl group into position 6′ of the substituted phenyl ring of benzotriazole derivatives **72** weakens the intramolecular hydrogen bond, and the molecule acquires a non-planar structure **73**, which hampers the ESIPT.[186]



e. Hydroxypyridines and hydroxyquinolines

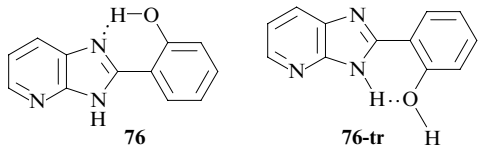
10-Hydroxybenzo[*h*]quinoline (**50**) and 10-hydroxy-5,6-dihydrobenzo[*h*]quinoline (**74**) undergo ESIPT both in non-polar and protic solvents.[187]



74 **75**

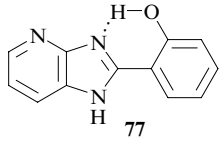
The long-wavelength fluorescence of the ESIPT tautomer, the ESIPT product, 2-(2-hydroxyphenyl)pyridine (**75**), was found only in frozen solutions in aprotic solvents. The absence of fluorescence of compound **75** in liquid solutions is attributed to deactivation of the ESIPT tautomer by the internal rotation mechanism, which is impossible in bound compounds **50** and **74**.[187] A study of the femtosecond dynamics of the ESIPT in molecule **50** provided the conclusion that the ESIPT in this molecule is barrierless.[188]

In solutions of 2-(2-hydroxyphenyl)-3*H*-imidazo[4,5-*b*]-pyridine (**76**) in aprotic solvents, the presence of two different rotamers (**76** and **76-tr**) was detected in the ground state.[189]



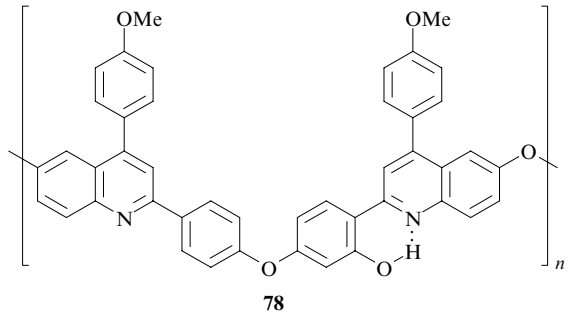
76 **76-tr**

Rotamer **76-tr** is responsible for the fluorescence with normal Stokes shift. The excitation of rotamer **76** gives rise to fluorescence with anomalous Stokes shift. The equilibrium between the two rotamers existing in the ground state is not established in the excited state, because the barrier to the isomer interconversion is higher in the excited state. Similar results were obtained for 2-(2-hydroxyphenyl)-1*H*-imidazo[4,5-*b*]pyridine (**77**).[190] The ESIPT was also observed for the cation obtained by protonation of compound **76**.[191]



77

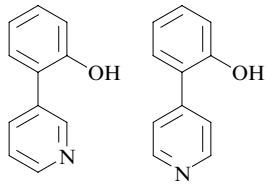
The excitation of polyquinoline-containing polymer **78** gives rise to the ESIPT.



78

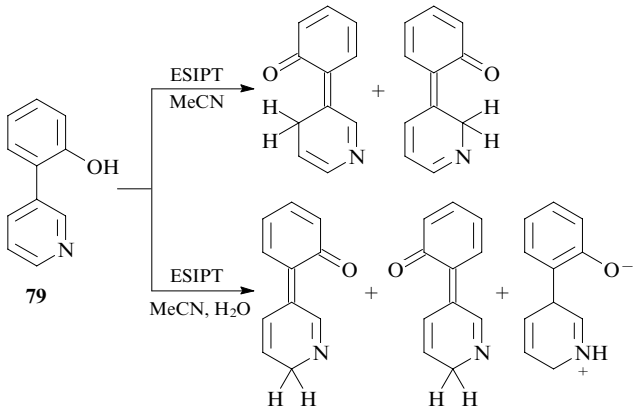
In a tetrachloroethane solution, the fluorescence spectrum exhibits bands for the enol and keto forms, while in the polymer film, fluorescence only for the keto form is observed.[192] The ESIPT time in the polymeric film is 55 fs and the ESIPT dynamics is 'monodisperse'. In liquid solutions, there is conformational inhomogeneity caused by different dihedral angles between the phenol and quinoline fragments and, as a consequence, by different lengths of the OH···N hydrogen bond. Elongation of the OH···N hydrogen bond gives rise to a barrier to the ESIPT, to a broad rate distribution of the ESIPT and to two-band fluorescence, as the rate of ESIPT depends considerably on the length of this bond. For about 30% of the molecules in a liquid solution, the ESIPT time is 130 fs and for other molecules, it is longer, *i.e.*, the ESIPT kinetics is polychronous.

In a study of the excited state proton transfer in the molecules of 2-, 3- and 4-(2-hydroxyphenyl)pyridines, it was found that 2-(2-hydroxyphenyl)pyridine (**75**) undergoes only the ESIPT from the hydroxy group to the pyridine nitrogen atom.[193]



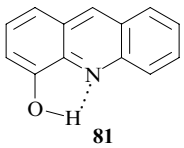
79 **80**

In the case of 3-(2-hydroxyphenyl)pyridine (**79**) and 4-(2-hydroxyphenyl)pyridine (**80**) in acetonitrile in the presence of water, both intra- and intermolecular (involving water molecule) excited state proton transfer both to the nitrogen atom and to the pyridine ring carbon atom takes place. The proportion of the ESIPT to the carbon atom measured based on inclusion of deuterium is determined by the amount of water in the solvent.



79

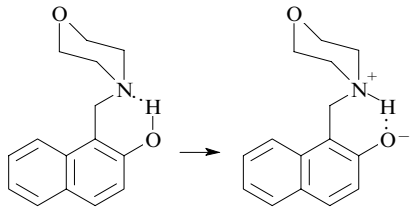
The 4-hydroxyacridine (**81**) molecule exists in the ground state as a five-membered intramolecular hydrogen-bonded complex in aprotic solvents and a solvated hydrogen-bonded complex in protic solvents.[194]

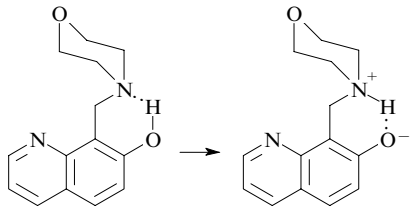


81

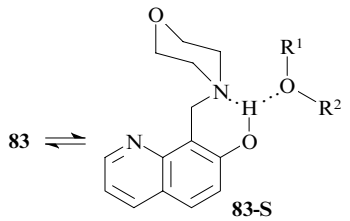
In non-polar aprotic solvents, 4-hydroxyacridine (**81**) does not fluoresce. In polar aprotic solvents and in reverse micelles, short-wavelength fluorescence of the hydrogen-bonded closed conformer appears. In protic solvents except for water, a broad fluorescence band for the solvated hydrogen-bonded complex is observed. In water, the fluorescence band of the solvated hydrogen-bonded complex is accompanied by weak long-wavelength fluorescence, which was assigned to the tautomer formed *via* excited state proton transfer through a solvent molecule. The calculation results indicate a low barrier to the ESIPT in the non-solvated molecule and barrierless excited state proton transfer involving a water molecule.

The excited state transfer in 2-hydroxy-1-(*N*-morpholinomethyl)naphthalene (**82**) in any solvent and 7-hydroxy-8-(*N*-morpholinomethyl)quinoline (**83**) in any solvent, except for proton-acceptor ones, affords ESIPT tautomers **82-T-1** and **83-T-1**, respectively.[195]



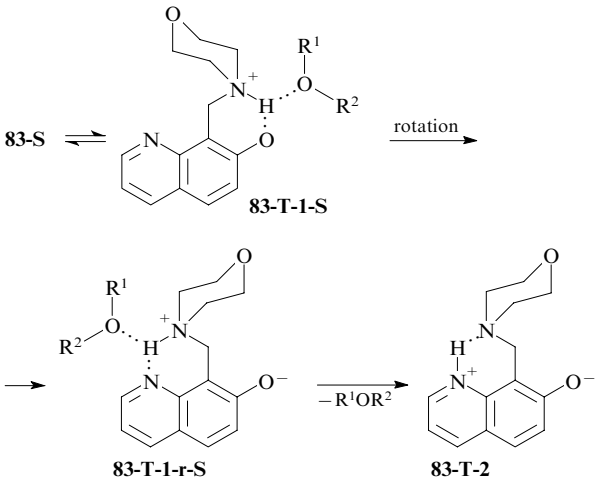


Bekker *et al.*[195] believe that in proton-acceptor solvents (R^1OR^2 = THF, dioxane), compound **83** exists as equilibrium between molecules with non-solvated hydroxy group (**83**) and molecules having an additional intermolecular hydrogen bond with the solvent (**83-S**).

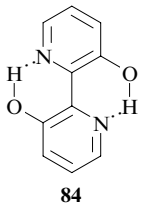


The excitation of molecules **83** and **83-S** results in ESIPT to give tautomers **83-T-1** and **83-T-1-S**. Due to the weak intramolecular hydrogen bond in molecule **83-T-1-S**, rotation of the protonated fragment is possible. In **82-T-1-r-S** formed upon this rotation, the ESIPT to the quinoline nitrogen atom takes place to give tautomer **83-T-2**.

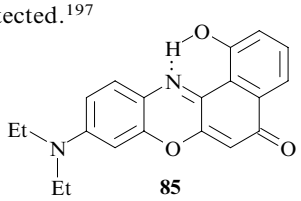
3,3′-Dihydroxy-2,2′-bipyridine (**84**) experiences double excited state proton transfer. The synchronous double transfer and the first step of the successive ESIPT occur in



50 fs; the second step occurs in 10 ps. No final conclusion about the ESIPT mechanism (synchronous or successive) was drawn.[196]



Two-band fluorescence of 9-diethylamino-1-hydroxybenzo[*a*]phenoxazin-5-one (**85**), *viz.*, 1-hydroxy-substituted Nile red, in the red and infrared spectral regions was detected.[197]



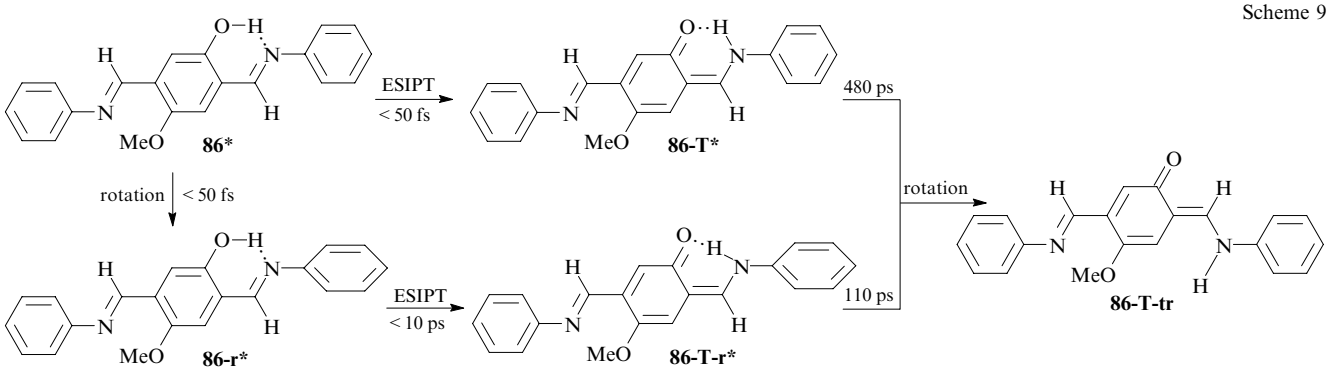
The infrared band with anomalous Stokes shift belongs to the ESIPT product. The ratio of the band intensities depends considerably on the solvent polarity. Unlike compound **85**, 2-hydroxy-substituted Nile red does not undergo ESIPT.

f. Schiff's bases

Unusual conformational effects were found in a study of the ESIPT in 4-methoxy-2,5-bis(phenyliminomethyl)phenol (**86**) and its analogues.[198–205]

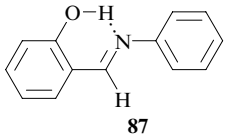
Excitation of the planar enol form induces two fast (< 50 fs) competing processes (Scheme 9): ESIPT giving planar keto conformer (**86-T***) and twisting of the enol form around the C—C bond between the central aromatic ring and the phenylimino group. A much slower (a temporal constant of 10 ps) ESIPT occurs in the twisted enol form **86-r*** to give non-planar keto conformer **86-T-r***. In both keto conformers (**86-T*** and **86-T-r***), rotation around the C=C bond between the central aromatic ring and the phenylimino group takes place (480 and 110 ps, respec-

Scheme 9



tively), resulting in the formation of the metastable photochromic *trans*-keto-tautomer **86-T-tr**.

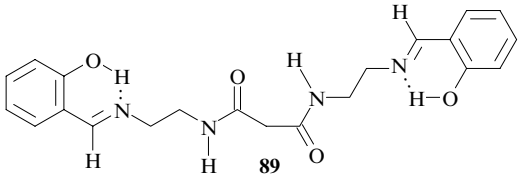
The broad band in the laser-induced fluorescence spectra without vibronic structure and in dispersed fluorescence spectra in a cooled *N*-salicylideneaniline (**87**) stream is caused, on the researchers' opinion,[199] by homogeneous broadening of the vibronic bands upon fast internal conversion $(\pi\text{-}\pi^*) \rightarrow (\text{n-}\pi^*)$ and the ESIPT. The dispersed fluorescence spectra exhibit two bands separated by 700 – 1000 cm^{-1}, which, according to the authors, is indicative of the formation of two keto tautomers upon the ESIPT. According to quantum chemical calculations, the ESIPT may produce three *cis*-keto forms of which two are non-planar and one is the planar *trans*-keto form.



87

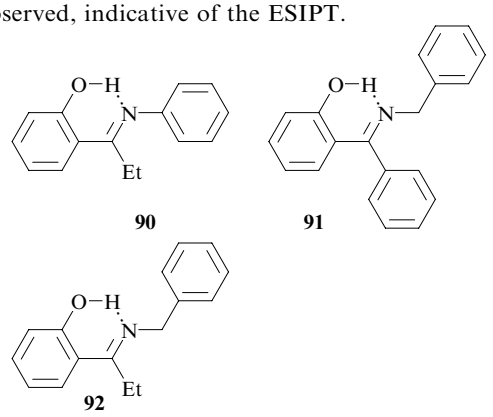
In *N*,*N*′-bis(salicylidene)-*p*-phenylenediamine (**88**) containing two intramolecular hydrogen bonds, ESIPT takes place at one of the bonds.[200] The ESIPT time is less than 50 fs. In the excited keto tautomer **^{1}88-T**, two competing processes take place (Scheme 10): deactivation to the ground state (**^{0}88-T**) and formation of the photochromic *trans*-keto form (**^{0}88-T-tr**). The time of the back proton transfer in the ground state is 0.5 – 1.5 ps.

The occurrence of ESIPT was established for *N*,*N*′-bis[2-*N*-salicylidene(amino)ethyl]malonodiamide (**89**) with two intramolecular hydrogen bonds. A two-step mechanism was proposed for this process (dienol – enol – keto – diketo) as opposed to the one-step (dienol – diketo) mechanism.[201]



89

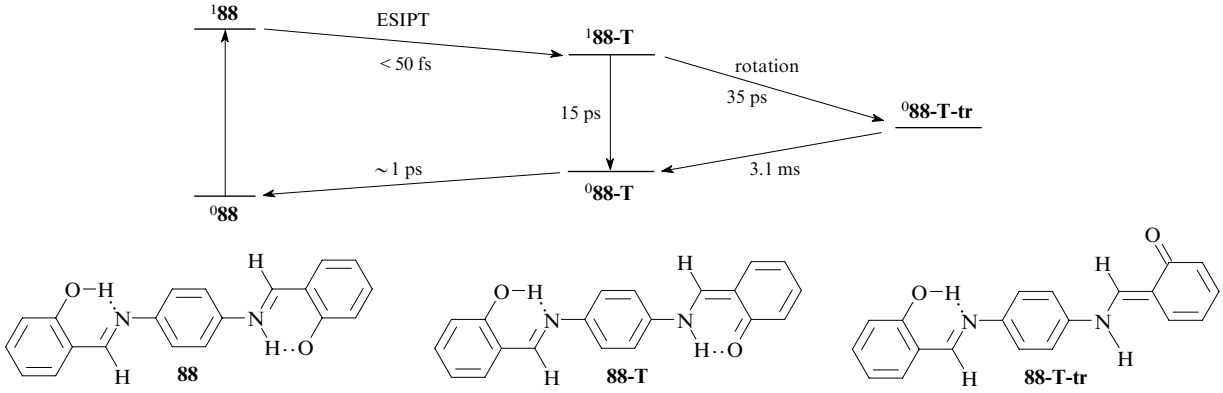
The intramolecular excited-state proton transfer was found in alcohol and aqueous solutions of 7-ethylsalicylideneaniline (**90**).[202] In liquid solutions of 7-phenylsalicylidenebenzylamine (**91**)[202] and 7-ethylsalicylidenebenzylamine (**92**),[203] fluorescence of ESIPT tautomers is absent. However, for solid and frozen (77 K) solutions of all three compounds, fluorescence with anomalous Stokes shift, was observed, indicative of the ESIPT.

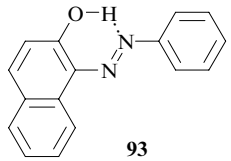


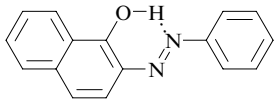
90 **91** **92**

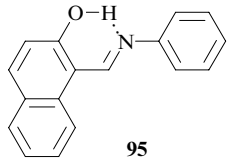
The excitation of aromatic azo dyes, 1-phenylazo-2-naphthol (**93**), 2-phenylazo-1-naphthol (**94**), and Schiff's bases, *N*-(2-hydroxy-1-naphthylmethylidene)aniline (**95**) and *N*-(1-hydroxy-2-naphthylmethylidene)aniline (**96**), with intramolecular hydrogen bond gives rise to ESIPT.[204]

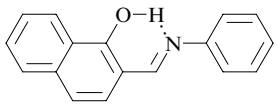
Scheme 10




93

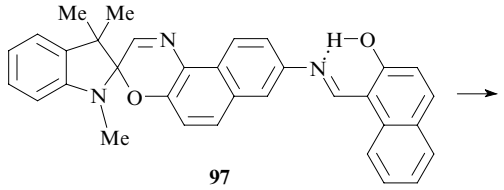

94

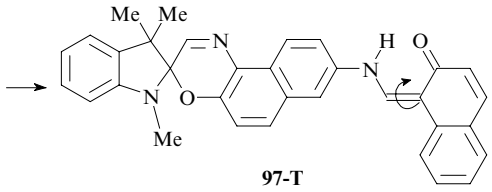

95

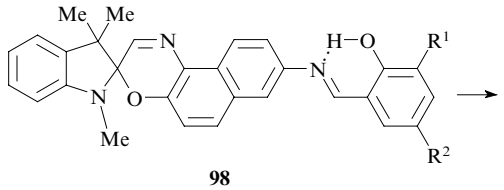

96

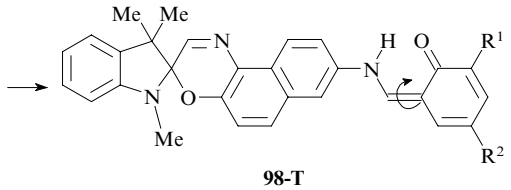
On excitation of the enol form, fast ESIPT occurs to give the tautomer. In all compounds, only the ESIPT tautomer produces fluorescence. The fluorescence quantum yield substantially increases with a decrease in the temperature. The introduction of electron-withdrawing or electron-donating groups in the *para*-position of the phenyl ring decreases the deactivation rate, which increases the fluorescence lifetime.

In spiro indolinonaphthoxazines **97** and **98**, the ESIPT has a rate constant of 1.25×10^{13} s^{-1} (Ref. 205). The resulting ESIPT tautomer is stabilized through rotation of the phenyl ring about the C–C bond (rate constant of 2.5×10^{12} s^{-1} for compound **97**). In parallel with the ESIPT, the C–O bond cleavage in the spironaphthoxazine fragment takes place.


97


97-T

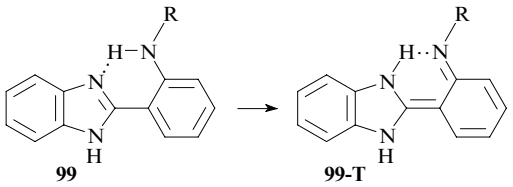

98


98-T

III. Excited state intramolecular proton transfer in hydrogen-bonded complexes of organic NH acids

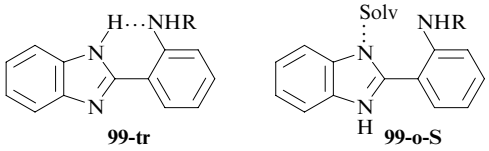
1. Complexes with the N–H···N⩽ bond

Solutions of 2-(2-aminophenyl)benzimidazoles **99** exhibit two-band fluorescence.[206–208]


99 **99-T**

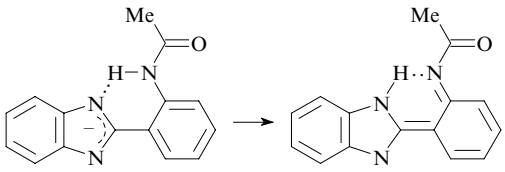
R = H (**99a**), Ac (**99b**), Bz (**99c**).

The fluorescence with a normal Stokes shift is caused by emission of rotamer **99-tr** (in aprotic solvents) and **99-tr** and **99-o-S** (in protic solvents).

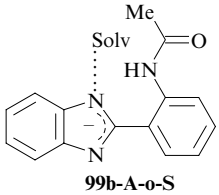

99-tr **99-o-S**

The long-wavelength fluorescence is caused by emission of the tautomer **99-T** formed upon the ESIPT of molecule **99**. The fluorescence intensity of the tautomer decreases with increase in the solvent polarity and proton-donor ability. Different lifetimes of the normal and tautomer fluorescence indicate, according to the authors,[206–208] that rotamers **99-tr** and **99-T** are not in equilibrium in the excited state. The relative intensity of the long-wavelength fluorescence band of compounds **99b** and **99c** is higher than in the case of **99a**. This is related to increase in the acidity of the amino group upon introduction of electron-withdrawing acetyl and benzoyl substituents.

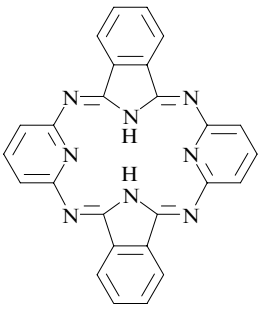
Two-band fluorescence of the 2-(2-acetamidophenyl)-benzimidazole monoanion (**99b**) in aqueous solutions was also observed.[209]


99b-A **99b-A-T**

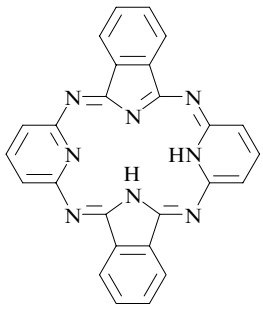
The long-wavelength fluorescence was assigned to the tautomer (**99b-A-T**) formed upon the ESIPT, while the short-wavelength fluorescence was attributed to the complex with the solvent (**99b-A-o-S**) in which no ESIPT takes place. According to the authors,[209] this was the first system where ESIPT was detected in the monoanion.


99b-A-o-S

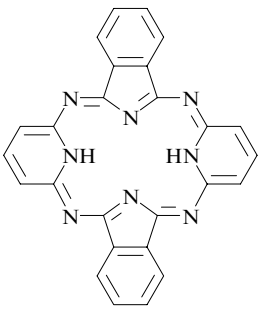
Hemiporphyrazine (**100**) (a phthalocyanine analogue with two opposing isoindole fragments of the molecule being replaced by two pyridine rings) can exist as three tautomers: **100**, **100-T-1** and **100-T-2**.[210]



100



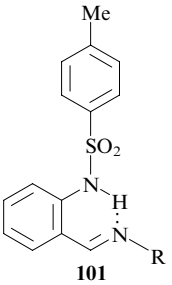
100-T-1



100-T-2

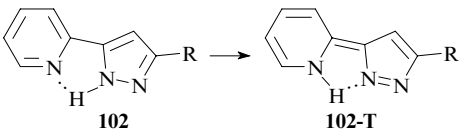
According to calculations, form **100** having absorption maxima at 338 (major) and 417 nm (shoulder) predominates in the ground electronic state. The fluorescence spectra recorded in dimethylformamide exhibit two bands with maxima at 420 and 675 nm. The short-wavelength fluorescence was assigned to emission of tautomer **100**, while the long-wavelength band was attributed to tautomer **100-T-2** resulting from the double ESIPT. According to calculations, tautomer **100-T-1** can be only an intermediate species with a short lifetime; therefore, it is barely seen in the fluorescence spectra.

The fluorescence with the anomalous Stokes shift in frozen glassy solutions of 2-(*p*-toluenesulfonylamino)benzylideneamine anils (**101**) was ascribed to the tautomer resulting from the ESIPT in the intramolecular complex with the $N-H\cdots N\leqslant$ hydrogen bond.[211] Unlike *o*-hydroxybenzaldehyde anils,[212] in compound **101**, the ESIPT is not followed by acoplanarization of the keto fragment.



101

Upon excitation of five-membered intramolecular complexes with the $N-H\cdots N\leqslant$ hydrogen bond, 5-(2-pyridyl)-1*H*-pyrazoles **102**, ESIPT takes place.[213]

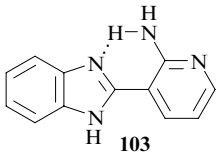


102 **102-T**

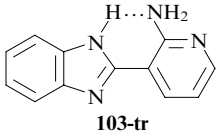
R = Py, Me, Bu^t, Ph.

The fluorescence spectrum exhibits two bands, the short-wavelength and long-wavelength ones, which correspond to forms **102** and **102-T**, respectively, and the short-wavelength fluorescence predominates. This was attributed to the existence of a considerable potential barrier in the excited state arising due to rearrangement of the molecular skeleton in the excited state.

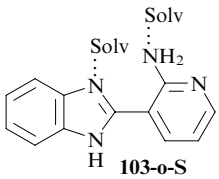
The two-band fluorescence of 2-(2-amino-3-pyridyl)-benzimidazole was accounted for by the existence of three rotamers, **103**, **103-tr** and **103-o-S**, in the ground state.[214]



103



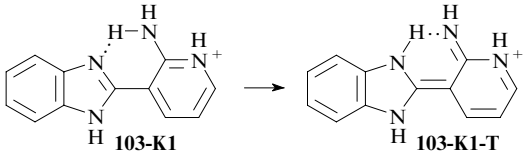
103-tr



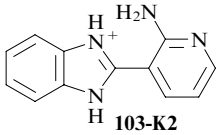
103-o-S

The short-wavelength fluorescence is emitted by rotamer **103-tr** in non-polar solvents and rotamer **103-o-S** in polar protic solvents. The long-wavelength fluorescence belongs to the tautomer formed from rotamer **103** upon ESIPT. The calculated activation energy of the conversion **103** → **103-tr** in the ground electronic state is 2.6 kJ mol^{-1}, and that in the excited state is 44.3 kJ mol^{-1}.

The fluorescence spectra of the 2-(2-amino-3-pyridyl)-benzimidazole monocation in water and in organic solvents and of the monoanion in water contain two bands.[215] In the ground state, two forms of the monocation exist: **103-K1** stable in polar solvents and **103-K2** stable in non-polar solvents. The short-wavelength fluorescence band comes from emission of form **103-K2**, and long-wavelength band belongs to form **103-K1-T** formed upon the ESIPT. No equilibrium is established between forms **103-K1** and **103-K1-T** in the excited state.

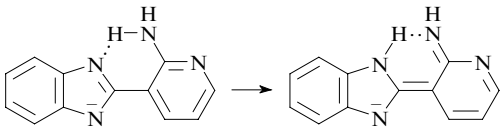


103-K1 **103-K1-T**



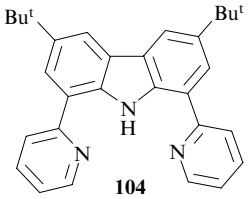
103-K2

The fluorescence spectra of the 2-(2-amino-3-pyridyl)-benzimidazole monoanion (**103-A**) in aqueous solutions exhibit two bands.[215] The short-wavelength fluorescence band is due to emission of the open solvated form, and the long-wavelength fluorescence is emitted by form **103-A-T** produced from **103-A** *via* ESIPT.



103-A **103-A-T**

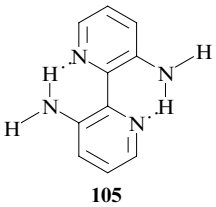
The fluorescence spectra of 4,7-di(*tert*-butyl)-2,9-di(2-pyridyl)carbazole (**104**) in non-polar and polar, protic and aprotic solvents exhibit two bands.[216] The coincidence of the excitation spectra of both fluorescence bands attests to the existence of only one form in the ground state. The long-wavelength band was assigned to the ESIPT tautomer. The short-wavelength band is related to emission of species that have not underwent ESIPT. A decrease in the rate constant for the ESIPT upon replacement of protium by deuterium attests to a contribution of the tunnelling mechanism in the ESIPT.



104

A considerable dependence of the radiationless deactivation of the ESIPT tautomer on temperature, solvent viscosity and replacement of protium by deuterium was noted.

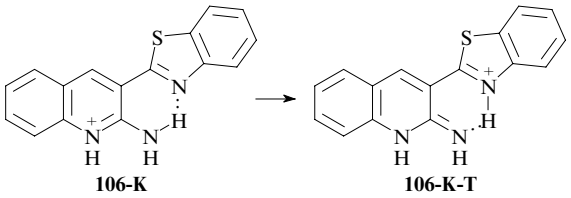
The excited state transfer in 3,3′-diamino-2,2′-bipyridine (**105**) follows two routes: (1) superfast double proton transfer (< 100 fs) followed by internal rotation (~250 fs); (2) combined double proton transfer and rotation (~250 fs).[217] This mechanism differs from that proposed for the ESIPT of 3,3′-dihydroxy-2,2′-bipyridine (**84**).



105

The vibrational relaxation in the ESIPT product takes 2–10 ps.

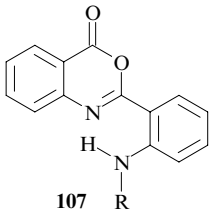
On excitation of the protonated 2-amino-3-(benzothiazol-2-yl)quinoline cation (**106**) in ethanol, two-band fluorescence is observed.[218] The long-wavelength fluorescence band was attributed to structure **106-K-T**.



106-K **106-K-T**

The excitation spectra of the two fluorescence bands are different, indicating the existence of at least two conformers in the ground state. The first conformer undergoes ESIPT to give a proton transfer species (long-wavelength band), while the second conformer does not undergo ESIPT (short-wavelength band). The ESIPT time measured by femtosecond absorption spectroscopy is equal to or less than 100 fs, which implies the existence of only one minimum on the potential energy surface of the excited state of the cation.

The fluorescence spectrum of N-substituted 2-(2-aminophenyl)-3,1-benzoxazin-4(4*H*)-ones (**107**) comprises two bands: a long-wavelength band with the anomalous Stokes shift, which corresponds to the emission of the ESIPT product, and a short-wavelength band emitted by the form where no excited-state proton transfer takes place.[219]

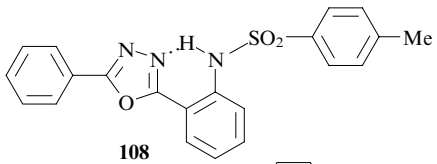


107

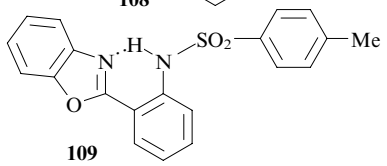
R = Ac, $COCCl_3$, Bz, $COCH_6H_4Me$, SO_2Me, $SO_2C_6H_4Me$-4, $CO_2C_6H_{13}$-n.

In the ground state, there is equilibrium between two planar rotamers, one having an N–H···N hydrogen bond in which ESIPT takes place and the other having an N–H···O bond where no ESIPT takes place. The fraction of the complex with the N–H···N$\leqslant$ bond increases with an increase in the proton-donor ability of the substituted amino group. According to *ab initio* quantum chemical calculations, the potential surface of the proton transfer in the first excited singlet state has a potential barrier of 2.1–26.8 kJ mol^{-1} depending on the electron-withdrawing properties of the substituent in the amino group.

Excitation of 2-(2-toluenesulfanylaminophenyl)-5-phenyl-1,3,4-oxadiazole (**108**) and 2-(2-toluenesulfanylaminophenyl)benzoxazole (**109**) in ethanol yields a species that generates laser radiation. This is formed upon ESIPT from the amino-group nitrogen atom to the oxadiazole (**108**) and oxazole (**109**) nitrogen atoms.[220]



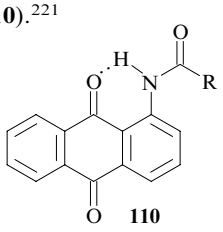
108



109

2. Complexes with the N–H···O=C$\leqslant$ bond

Systems with ESIPT from nitrogen to oxygen are few in number. The excited state intramolecular proton transfer of this type was detected in 1-(acylamino)anthraquinones (**110**).[221]

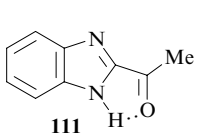


110

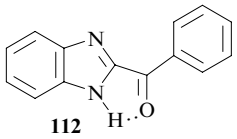
R = n-C_6H_{13}, CH_2Cl, $CHCl_2$, CF_3.

The duration of the excited state proton transfer estimated from the time of tautomer fluorescence buildup is ~300 fs, *i.e.*, it is shorter than the solvent relaxation time. The efficiency of ESIPT increases with increase in the electron-withdrawing ability of the substituent R. According to the authors,[221] the ESIPT is an equilibrium process occurring by a tunnelling mechanism.

On the basis of the measured Stokes shift of the fluorescence spectra of 2-acetylbenzimidazole (**111**) and 2-benzoylbenzimidazole (**112**) in hydrocarbon solvents, the authors[222] concluded that ESIPT does take place in these compounds. The excited state proton transfer can take place upon excitation of the closed conformer, a five-membered hydrogen-bonded intramolecular complex. However, this conclusion casts doubt, because the Stokes shift of the fluorescence spectra given by the authors is rather low.



111

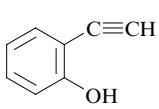


112

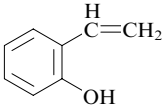
In protic solvents, excited state intermolecular proton transfer to the solvent molecule is more efficient, probably, due to weak intramolecular hydrogen bond.[223]

IV. Excited state intramolecular proton transfer in the O—H···π-system complexes

A number of publications of the last decade deal with the excited state intramolecular proton transfer from the OH group on the carbon atom.[224–232] 2-Hydroxyphenylacetylene (**113**)[224] and 2-hydroxystyrene (**114**)[225] are the first compounds where ESIPT from the hydroxy group to the carbon atom was detected.



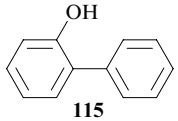
113



114

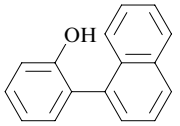
On excitation in an aqueous solution, these compounds undergo ESIPT from hydroxy group to the β-carbon atom to give the corresponding tautomer, *o*-quinone methide.

The excited-state proton transfer from the OH group onto the sp^2-hybridized carbon atom of the aromatic ring occurs in the 2-phenylphenol molecule (**115**).[226, 227]

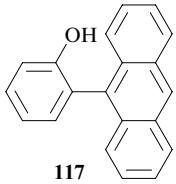


115

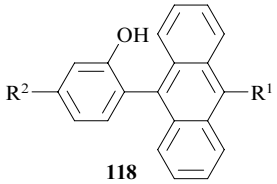
The ESIPT process was detected based on the H/D exchange and on the appearance of a long-wavelength fluorescence band for water-containing solutions. It was assumed that the ESIPT may involve only *o*-hydroxybiaryls in whose molecules the internal rotation of fragments is possible in the ground state. Due to rotation, the s-orbital of the proton of the hydroxy group overlaps with the acceptor π-system to give a weak hydrogen bond in the ground state, the presence of this bond being a necessary condition for the excited state proton transfer. Similar results were obtained for 2-(1-naphthyl)phenol (**116**) in acetonitrile with addition of water[228] and for 9-(2-hydroxyphenyl)anthracene (**117**) in acetonitrile,[229] as well as for four its derivatives **118**.[230] In all of these cases, water is also needed.



116



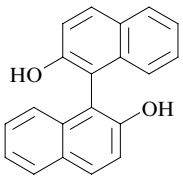
117



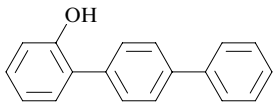
118

R^1 = H, R^2 = OH;
R^1 = Me, R^2 = H;
R^1 = Ph, R^2 = H;
R^1 = 4-OHC_6H_4, R^2 = H.

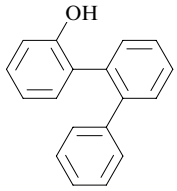
In 1,1′-bis(2-naphthol) (**119**) molecule, the excited state proton transfer occurs from the hydroxy group to the carbon atom of the naphthyl rings,[231] while in 2-hydroxy[1,1′;4′,1″]terphenyl (**120**), 2-hydroxy[1,1′;2′,1″]terphenyl (**121**) and 2-(2-hydroxyphenyl)-9*H*-fluorene (**122**) molecules, the transfer is to the carbon atoms of the terphenyl and fluorenyl rings.[232]



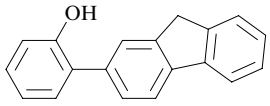
119



120



121



122

According to the authors,[231, 232] the excited-state proton transfer on the carbon atom may both be intramolecular and occur through a chain of water molecules. However, there is no convincing experimental proof for the direct intramolecular transfer in dry aprotic solvent. In all cases, for the ESIPT to proceed, the presence of water or other protic solvent is required, and so-called water relay excited state transfer mechanism is implemented.

V. Conclusion

Analysis of publications presented in this review demonstrates that studies of the excited state intramolecular proton transfer is the area still attracting the attention of many researchers. The fast adiabatic excited state proton transfer is followed by structural and electronic changes in the molecule, resulting in the formation of the excited tautomer the fluorescence of which shows an anomalous Stokes shift. These unusual photophysical properties deter-

mine a number of important applications of ESIPT systems. Considering published data on the conformational effects in ESIPT reactions attests to a substantial effect of the conformations on the transfer mechanism. The elucidation of the true mechanism of ESIPT requires thorough conformational analysis of ESIPT systems, determination of the structures of possible rotamers and solvates.

One more important conclusion drawn from analysis of the published data is that the general mechanism of ESIPT is determined by not only kinetic parameters of the proper proton transfer but is also considerably affected by the equilibrium processes in the ground electronic state. As a result, the experimentally observed two-band fluorescence of a solution of a compound with intramolecular hydrogen bond does not mean an acid–base equilibrium in the excited state but arises due to the existence of different rotamers in the ground electronic state, which occur in a conformational equilibrium.

The femtosecond studies of systems with a strong hydrogen bond carried out in the last two decades confirm the generally accepted view stating that in most systems with intramolecular hydrogen bond, ESIPT is a fast barrierless and non-equilibrium process. However, as shown in some works, in systems with weaker hydrogen bonds, a barrier to the ESIPT may exist, related to the conformational processes in the excited state.

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