Excited-State Intramolecular Proton Transfer: A Short Introductory Review

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Abstract: In this short review, we attempt to unfold various aspects of excited-state intramolecular proton transfer (ESIPT) from the studies that are available up to date. Since Weller’s discovery of ESIPT in salicylic acid (SA) and its derivative methyl salicylate (MS), numerous studies have emerged on the topic and it has become an attractive field of research because of its manifold applications. Here, we discuss some critical aspects of ESIPT and tautomerization from the mechanistic viewpoint. We address excitation wavelength dependence, anti-Kasha ESIPT, fast and slow ESIPT, reversibility and irreversibility of ESIPT, hydrogen bonding and geometrical factors, excited-state double proton transfer (ESDPT), concerted and stepwise ESDPT.

Keywords: tautomerism; proton transfer; excited-state; spectroscopy

1. Introduction

Excited-State Proton Transfer (ESPT) is an important reaction that controls the functioning of various biological systems [1–9]. Probe molecules in various biological systems, based on this mechanism, have also been suggested recently [10,11]. Moreover, ESIPT systems have found applicability in sensors for humidity [12,13], luminescent solar collectors [14], proton transfer lasers [15–19], photo stabilizers [20], devices based on thermally activated delayed fluorescence [21,22], white light generation [23–25], organic light-emitting diodes (WOLED) [26] as well as suitability in sensing of anion and cations [27–30], photochromic switching [31,32] and even understanding of fading of colorants in art [33].

As a general definition, molecules, which have both proton (hydrogen) donating/accepting groups, can undergo excited-state intramolecular proton transfer (ESIPT) due to increased acidity/basicity. In salicylic acid (SA), for example, the hydroxyl hydrogen becomes more electropositive whereas the carboxylic oxygen attains more electronegative character in the excited-state. This results in proton translocation from the hydroxyl group to the carboxylic group. A more general schematic representation of ESIPT in SA is given in Scheme 1. Here N and T are the ground state normal and tautomer (obtained as a result of the ESIPT) forms, respectively. Their excited state analogues are denoted as N* and T*. This translocation may be complete resulting in zwitterion [34,35] involving electron transfer and in some cases, it is displaced, resulting in partial or complete hydrogen transfer (ESIHT). A clear distinction between ESIHT and ESIPT is pointed out by Waluk [36].

Traditionally, ESIPT is considered as a process where the proton is exchanged through intramolecular hydrogen bonding between the proton donating and accepting groups in the molecule. There are also systems, where the proton donating and accepting sites are not adjacent and hence the proton is transferred over a long distance. In this particular case, the PT can be either solvent or concentration assisted and as a net effect a proton is transferred in the same molecule, termed as pseudo-intramolecular [37].
The families of hydroxy carboxylic acids that have been exploited as proton transfer systems are hydroxyl-benzoic acids and esters \([34,35,38–70]\), hydroxynaphthoic acids \([71–75]\) and anthranilic acid and its esters \([76–81]\). Besides carboxylic acids, other compounds belonging to hydroxyflavones \([82–84]\), quinoline family and anthraquiniones \([85–100]\), 7-azaindole and derivatives, hydroxyl phenyl benzoxazole (HBO) derivatives \([100–119]\). Azo dyes and Schiff bases \([120–124]\) were extensively studied and are well documented in the literature. Some other notable systems have also been the subject of interest \([124–131]\). A summary of some of the most frequently used experimental methods is given in \([3]\).

Experimentally, ESIPT can be traced out by the appearance of large Stokes shifted emission. The ESIPT process can be probed by steady-state as well as time-resolved measurements \([124]\). As ESIPT occurs in femtosecond scale, in most of the cases its time evolution can be studied by fluorescence up conversion technique \([84,125]\) or from line width information from Shpol’skii matrices \([83]\). For slower ESIPT, time-correlated single photon counting (TCSPC) can provide information about its dynamics.

The aim of the present review is to assess the main aspects regarding ESIPT dynamics. For this reason, this thematic article is divided into the following sections, where some important developments in the field of ESIPT are discussed:

1. Fast and slow ESIPT vis a vis irreversible and reversible ESIPT
2. Effect of substitution, hydrogen bonding and geometrical effects
3. Excited-state double proton transfer (ESDPT), proton relay, concerted/stepwise proton transfer
4. Excitation wavelength dependence, anti-Kasha ESIPT, anti-aromaticity
5. Ground state vis a vis excited-state tautomerisation

2. Fast and Slow ESIPT

In his pioneering work, Weller suggested that there is an asymmetric double-well potential (Figure 1) for the ESIPT in SA and its derivative methyl salicylate (MS) to explain the observed normal (with small Stokes shift) from P* and large Stokes shifted emission resulting from the tautomer T* after ESIPT \([34,35]\).

Scheme 1. Representative photocycle of excited-state intramolecular proton transfer (ESIPT) in salicylic acid (SA).
Figure 1. Asymmetric double-well potential for ESIPT in SA and methyl salicylate (MS) proposed by Weller (reproduced by permission from reference [63]). Reprinted with permission from (Maheshwari, S.; Chowdhury, A.; Sathyamurthy, N.; Mishra, H.; Tripathi, H.B.; Panda, M.; Chandrasekhar, J. Ground and Excited-state Intramolecular Proton Transfer in Salicylic Acid: An Ab Initio Electronic Structure Investigation. J. Phys. Chem. A 1999, 103, 6257–6262). Copyright (1999) American Chemical Society.

However, later, careful excitation spectra as well as time-resolved studies revealed that the concept of double-well potential was not correct in these cases, and in fact, normal and tautomer emissions result from two different conformers—one with a proper intramolecular hydrogen bond (IHB) to undergo ESIPT (P form) resulting in T form and the other lacking this strong IHB and giving rise to normal emission (R form) [63] as shown in Figure 2. The emission from the T form has a large Stokes shift whereas normal emission from the R form has a rather small Stokes shift. Moreover, the excitation spectrum corresponding to the emission from R form is red-shifted as compared to the excitation spectrum corresponding to T form [50,53]. Time-resolved studies showed that ESIPT is very fast [40] and occurs in the fs scale, which is now considered as a typical feature of this phenomenon [40,83,84].

However, some studies suggested a slow ESIPT occurring in certain molecules. Alarcos et al. [105] reported that due to intramolecular charge transfer (ICT), the proton transfer is slowed down in 6-amino-2-(2′-hydroxyphenyl)benzoxazole (6A-HBO) and its methylated derivatives and occurs in picosecond time scale. In the case of methanol, it has been found to be assisted by solvent molecules and occurs through tunneling as a large kinetic isotope effect (KIE) of about 13 is observed. Joshi et al. [89] found that ESIPT is rather slow in 3-hydroxyisoquinoline (3-HQ) and can be observed in nanosecond scale depending on solvent polarity. An illustration of this is shown in Figure 3.
Figure 2. P, R and T forms of SA from reference [63]. Reprinted with permission from (Maheshwari, S.; Chowdhury, A.; Sathyamurthy, N.; Mishra, H.; Tripathi, H.B.; Panda, M.; Chandrasekhar, J. Ground and Excited-state Intramolecular Proton Transfer in Salicylic Acid: An Ab Initio Electronic Structure Investigation. J. Phys. Chem. A 1999, 103, 6257–6262). Copyright (1999) American Chemical Society.

Figure 3. Illustration of solvent-dependent ESIPT in 3-HQ (the potential barrier is increased in case of aprotic polar solvent as compared protic polar) from ref [89].

Slow proton transfer dynamics in the nanosecond scale was also reported for 1-(2-hydroxy-5-chloro-phenyl)-3,5-dioxo-1H-imidazo-[3,4-b]isoidol(ADCL) by Ray et al. [95]. Khimich et al. [93] have shown that 2-amino-3-(2’-benzoxazolyl)-quinoline (ABO) upon protonation exhibits dual fluorescence resulting from initial tautomer and ESIPT product. Moreover, the cation has a significant potential barrier which decreases with an increase in basicity according to the theoretical calculations.

In 3-hydroxychromene (3-HC), intermolecular interactions have been found to slow down the ESIPT reaction considerably [94]. ESIPT process in 3-hydroxy-2-methylbenzo[g] quinolin-4(1H)-one (MBQ) was studied by Zamotaiiev et al. [86] who found that reversible ESIPT with a rather long time scale (ns) takes place. Liu et al. [92] investigated ESIPT in a series of molecules bearing a 2,11-dihydro-1H-cyclopenta[de]indeno[1,2-b]quinoline (CPIQ) chromophore and found that ESIPT is irreversible with a significant barrier (kinetic-control regime). Moreover, ESIPT can be tuned by the substituent. The representative reaction is demonstrated in Figure 4.
Figure 4. Effect of substitution on ESIPT in 2,11-dihydro-1H-cyclopenta[de]indeno[1,2-b]quinoline (CPIQ) from ref. [92]. Reprinted with permission from (Liu, Z.-Y.; Hu, J.-W.; Huang, T.-H.; Chen, K.-Y.; Chou, P.-T. Excited-State Intramolecular Proton Transfer in the Kinetic-Control Regime. Phys. Chem. Chem. Phys. 2020, 22, 22271–22278). Published by the PCCP Owner Societies.

Ni et al. [97] modelled the effect of substitution on ESIPT behaviour in 4′-(2-hydroxybenzylidene)-1,2-dimethyl-1H-imidazol-5(4H)-one (o-LHBDI) derivatives by DFT and TD-DFT methods. They found that the ESIPT barrier decreases when the substituent has a stronger electron-withdrawing ability or weaker electron-donating ability. Zhang et al. [96] investigated ESIPT on “naked” diazaborepins and found that ESIPT is prohibited with an increase in solvent polarity. Solvent-dependent ESIPT and ground state intramolecular proton transfer (GSIPT) has been reported by Kuang et al. in 4′-N,N-diethylamino-3-hydroxyflavone (DEAHF) [90]. They used femtosecond pump–dump probe spectroscopy to prepare short-lived grounds state tautomers and monitor the GSIPT process. Moreover, GSIPT has been found to be an irreversible two-state process. A representative diagram showing ESIPT and GSIPT is shown in Figure 5.

Figure 5. Solvent polarity effect on ESIPT and ground state intramolecular proton transfer (GSIPT) in 4′-N,N-diethylamino-3-hydroxyflavone (DEAHF) from ref [90]. Reprinted with permission from (Kuang, Z.; Guo, Q.; Wang, X.; Song, H.; Maroncelli, M.; Xia, A. Ultrafast Ground-State Intramolecular Proton Transfer in Diethylaminohydroxyflavone Resolved with Pump–Dump–Probe Spectroscopy. J. Phys. Chem. Lett. 2018, 9, 4174–4181). Copyright (2018) American Chemical Society.
3. Hydrogen Bonding, Effect of Substitution and Crystal Structure

ESIPT reaction has been found to depend on external hydrogen bonding with the molecule. In SA, external hydrogen bonding with diethyl ether (Et₂O) breaks the existing dimers and only monomeric emission from tautomer has been observed with enhanced intensity [51]. The effect of substitution on SA was studied extensively, indicating the ESIPT dependence. Lahmani and Zehnacker-Rentien [54] studied the effect of methyl and methoxy substitution at the para position of the hydroxyl group in SA. They found that methoxy salicylic acid (5-MeOSA) shows only normal emission (~400 nm) but dual emission including emission from tautomer (500 nm) is observed in the presence of hydrogen bonding diethyl ether and suggested that hydrogen bonding promotes ESIPT reaction. Smoluch et al. extended the study with time-resolved measurements for 5-MeOSA and suggested a geometric change on excitation. Table 1 shows the decay data of 5-MeOSA. It can be seen that there is a rising component in the decay profile of tautomer emission at 298 K which, however, is not evident at 160 K. Instead a mono-exponential decay is observed. The presence of rising component at 298 K has been attributed to excited-state equilibrium between normal and tautomer emissions which apparently is not present at 160 K. These observations indicate that besides hydrogen bonding, molecular geometry also plays an important role in ESIPT. Fluorescence properties of the salicylic anion have also been found to be modulated considerably depending on electron donor/acceptor substituents [66]. In polymer matrix (PMMA), SA has been found to exhibit only B emission arising from tautomer (T) after ESIPT. The absence of dimer is ascribed to hydrogen bonding with the polymer [51]. However, it shows a bi-exponential decay throughout the emission profile indicating the effect of heterogeneity in polymeric media. Again these observations point to the fact that both hydrogen bond and its geometry play an important role in ESIPT.

Table 1. Fluorescence decay parameters of 5-MeOSA-Et₂O complex. (τ₁ and τ₂ are decay rising components and α₁ and α₂ are corresponding amplitudes).

| Temperature | Emission Wavelength nm | τ₁ ns | τ₂ ns | α₁ | α₂ | χ² |
|-------------|------------------------|-------|-------|-----|-----|-----|
| 298 *       | 400                    | 0.4   | 2.32  | 51.52 | 48.58 | 1.04 |
| 298 *       | 500                    | 0.43  | 2.42  | −5.27 | 14.41 | 1.09 |
| 160 **      | 400                    | 2.51  | 11.54 | 31.55 | 68.45 | 1.0  |
| 160 **      | 500                    | -     | 11.50 | -    | -    | 1.05 |

From: * decay data are shown in the corresponding channel from reference [55]; ** unpublished decay data.

Parada et al. [98] reported the influence of hydrogen bond geometry on the dynamics of ESIPT in phenol-quinoline compounds. They found that long donor-acceptor distance increases the PT barrier whereas a large dihedral angle (angle between the planes having proton donor-acceptor subunits) results in a deactivation channel after ESIPT. Hydrogen bonding wires/bridge formation has been reported to be a prerequisite for ESIPT in quinolone derivatives, where proton donor and acceptor groups are not adjacent. 6-hydroxyquinoline (6-HQ) and 7-hydroxyquinoline (7-HQ) have been found to undergo ESIPT in water, methanol: water and acetic acid through hydrogen bridge formation [99,101–104]. Although the proton is transferred through intermolecular hydrogen bonding(s) the process as a net effect can be considered as intramolecular. Therefore, these can be considered as cases of solvent-assisted pseudo intramolecular excited-state proton transfer.

Hristova et al. [87,88] studied ESIPT in 10-hydroxybenzo(h)quinolone (HBQ) and structurally modified compounds. They found that keto tautomer is observed when electron acceptor substituents are present at position 7 of the HBQ backbone. Theoretical modelling suggested that the substitution results in a transition from a single well to double
minimum potential. They have attributed it to the charge transfer character imparted by the substituent.

Effect of different substituted groups on ESIPT in 1-(acylamino)-anthraquinones (AAQ’s) was studied theoretically by Ma et al. [126]. They reported that hydrogen bond strengthening was followed by ESIPT depending on the potential energy barrier of a particular derivative. Theoretically computed potential energy surfaces (PES) are shown in Figure 6. It can be seen that the potential barrier in the S$_1$ state is significantly affected by substitution.

Figure 6. Theoretically estimated potential energy surfaces for AAQ’s (reproduced from reference [126]. Reprinted with permission from (Ma, Y.; Yang, Y.; Lan, R.; Li, Y. Effect of Different Substituted Groups on Excited-State Intramolecular Proton Transfer of 1-(Acylamino)-Anthraquinons. J. Phys. Chem. C 2017, 121, 14779–14786). Copyright (2017) American Chemical Society.

The effect of intermolecular interactions on excited-state intramolecular proton transfer (ESIPT) in 4’-N,N-dimethylamino-3-hydroxyflavone (DMHF) doped in acetonitrile crystals was studied by Furukawa et al. [85]. They found prominent differences in two different crystalline phases which are explained by modulation of the potential energy surface (Figure 7). In a recent work, the structure–property relationship on the ESIPT mechanism from the viewpoint of the design of efficient solid-state emitters is elucidated. They have demonstrated that besides restricting the nonradiative pathways, an efficient ESIPT is also essential for efficient emitters [106].
Double Proton Transfer Mechanism of 7-Azaindole Dimer in Solution. [85]. Solid and dotted lines show potential energy curves for low and high-temperature crystalline phases respectively. Reprinted with permission from (Furukawa, K.; Yamamoto, N.; Hino, K.; Sekiya, H. Excited-State Intramolecular Proton Transfer and Conformational Relaxation in 4′-N,N-Dimethylamino-3-Hydroxyflavone Doped in Acetonitrile Crystals. Phys. Chem. Chem. Phys. 2016, 18, 28564–28575). Published by the PCCP Owner Societies.

4. Excited-State Double Proton Transfer (ESDPT), Proton Relay, Concerted/Stepwise Proton Transfer

ESDPT is also considered to represent typical cases of concentration-assisted ESIPT occurring in dimers. ESDPT can be traced back to the work of Taylor et al. [107] in 7-azaindole (7-AI) which they attributed to cooperative biprotonic reversible proton transfer. Since then, several studies were done to elucidate the presence of ESDPT [108–114,127–131]. Figure 8 shows 7-AI monomer, dimer and tautomer formed by ESDPT. The proton transfer time was found to be rather short (ps time scale) [109]. The ESDPT process can occur either in a stepwise manner or through a concerted mechanism (illustrated in Figure 9). By femtosecond time-resolved measurements, Douhal et al. [110] suggested that in 7-AI, ESDPT takes place in a stepwise manner. The mechanism remained controversial [111,112] until new experimental as well theoretical findings indicated that it occurs in a concerted fashion. From time-resolved measurements, Takeuchi and Tahara [113] concluded that ESDPT in 7-AI dimers takes place in a concerted manner in 1.1 ps time. By using a proper topological description of the 7-AI dimer in the gas phase, Crespo-Otero et al. [114] suggested that stepwise ESDPT is not favorable due to kinetic and thermodynamical reasons.

Figure 7. Modification of potential energy surface (PES) by crystalline phases of acetonitrile from reference [85]. Solid and dotted lines show potential energy curves for low and high-temperature crystalline phases respectively. Reprinted with permission from (Furukawa, K.; Yamamoto, N.; Hino, K.; Sekiya, H. Excited-State Intramolecular Proton Transfer and Conformational Relaxation in 4′-N,N-Dimethylamino-3-Hydroxyflavone Doped in Acetonitrile Crystals. Phys. Chem. Chem. Phys. 2016, 18, 28564–28575). Published by the PCCP Owner Societies.

Figure 8. 7-AI monomer, dimer and tautomer forms from reference [113]. Reprinted with permission from (Takeuchi, S.; Tahara, T. The Answer to Concerted versus Step-Wise Controversy for the Double Proton Transfer Mechanism of 7-AzaIndole Dimer in Solution. Proceedings of the National Academy of Sciences 2007, 104, 5285–5290). Copyright (2007) National Academy of Sciences, U.S.A.
A detailed account of ESDPT has also been reported recently showing that some systems appear to favour stepwise ESDPT mechanism [115]. For ESDPT in 2-aminopyrene/acetic acid (2-AP) system, three types of ESDPT are suggested. Besides concerted, stepwise 1 and stepwise 2 ESDPT (depending on the sequence of proton transfers) are pointed out. From their calculations, they found that the first proton transfer is barrierless (stepwise 1) whereas a high barrier exists for concerted and stepwise 2 processes.

In another work, the ESIPT mechanism in 2-(2-hydroxyphenyl)benzoxazole (HBO), bis-2,5-(2-benzoxazolyl)-hydroquinone (BBHQ) and 2,5-bis(5′-tert-butyl-benzoxazol-2′-yl)hydroquinone (DHBO) were investigated using time-dependent density functional theory (TDDFT). The possibility of simultaneous ESDPT or successive proton transfers besides single proton transfer is reported [128].

The ESDPT mechanism in 2,2′-Bipyridyl-3,3′-diol (BP(OH)2) has been examined theoretically by Zhao et al. [129] in different polar aprotic solvents and found that solvent can regulate and control the ESDPT process. Plasser et al. [130] studied the ESDPT process in BP(OH)2 by second-order approximate coupled-cluster (RI-CC2) and time-dependent density functional theory (TDDFT) and suggested that concerted process in this molecule is highly unlikely as it proceeds along a ridge in the S1 excited-state and advocated for stepwise mechanism.
The other notable compound is SA which also forms cyclic dimers in the crystalline state. Pant et al. [46] suggested that ESDPT may be responsible for the tautomer emission. Bisht and co-workers in a supersonic jet study also reported the possibility of double proton transfer in excited-state [50]. Later studies also confirmed the tautomer emission in dimers, but could not find the evidence of ESDPT in SA systems [47,48,61]. Young et al. suggested a conical intersection (CI) in the case of 5-fluorosalicylic acid dimer [48]. In view of these studies to further explore the ESDPT mechanism from both theoretical as well as experimental points of view will be interesting.

Other interesting examples of tautomerization are porphycenes which exhibit ground as well as excited-state double proton transfer [131]. This is manifested in depolarized emission, viscosity-dependent radiationless deactivation and vibrational mode-specific tunneling splitting.

5. Excitation Wavelength Dependence

Excitation wavelength dependence on the excited-state proton transfer was first reported by Hetherington et al. in 7-azaindole [98,109]. They found that excited-state double proton transfer occurs in less than 5 ps at room temperature, but exhibits excitation wavelength dependence at 77 K which could be explained on the basis of a double-well potential. The investigation suggests that direct (from the initially excited state) and indirect (from the relaxed excited state) emissions take place which explains the presence of slow component at 77 K. Pant et al. [46] investigated the excitation wavelength dependence in SA solid. Two fluorescence bands U (~370 nm) and B (~450 nm) are observed. They attributed U emission to the molecules to the dimer molecules which do not undergo ESIPT whereas the B emission which has a large Stokes shift arising from ESIPT. They found that at room temperature as well as for shorter excitation wavelengths at 77 K, the ratio of U to B intensities remains unchanged. However, at 77 K and for longer wavelength excitation, the B emission changes drastically. Further, the decay for both normal and tautomeric emissions is exponential with identical decay times at higher temperatures as well as for shorter wavelengths of excitation. This indicates that there exists a fast excited-state equilibrium between normal and proton transferred forms. The presence of ground state tautomers and fast inter-conversion was suggested as a possible reason. In a later study, Denisov et al. [47] also investigated temperature and excitation wavelength dependence in SA and dihydroxybenzoic acid (DHBA) and possibilities for explaining this behaviour were pointed out. They pointed out that for a self-consistent interpretation of observations, the excited state of the dimer may have double-well potential with a rather high barrier. This may arise from the organization of the dimer geometry upon excitation. However, to address the temperature and excitation wavelength dependence a comprehensive theoretical study is still lacking and needs to be explored further. The role of anti-aromaticity on ESIPT has also been elucidated in a recent work [49]. It has been suggested that SA is aromatic in $S_0$ and $S_2$ states but the ESIPT can occur only from $S_1$ state, which is antiaromatic. This should be an interesting aspect if this holds for SA dimers also.

Recently renewed interest in the excitation wavelength dependence of the ESIPT emerged in the literature [116–118]. Excitation wavelength dependence on the ESIPT emission was observed and reported as anti-Kasha ESIPT (Figure 10). As Kasha’s rule states that emission originates from the lowest excited singlet state, the ESIPT emission is observed from the lowest excited state of tautomer after undergoing ESIPT from normal molecule to the $S_1$ state of tautomer.
Moreover, some theoretical attempts have also been made to explain the excitation wavelength dependence [118]. They have attributed the increased quantum yield from the tautomer emission as a result of anti-Kasha ESIPT. It appears, as shown in Figure 11, to be a potential energy surface crossing between the S2 state of the normal molecule and S1 state of the tautomer. It is clearly evident that from higher excited-states ESIPT is enhanced, however, terming it as anti-Kasha is debated [119].
6. Ground State vis a vis Excited-State Tautomerization

Certain categories of molecules, such as azo dyes and Schiff bases, have also been found to form tautomers in both ground and excited states [120–124].

As these systems involve both ground and excited tautomerisation [132] (as sketched by Scheme 2), the efficiency of tautomerization in the excited state is an important parameter. In these works, the authors estimated the efficiency of tautomerization from the excitation spectra. Accordingly, in the case of ESIPT, the excitation spectrum will have a contribution from both enol-like (A) and keto-like (H) forms with emission coming only from the H tautomer. In this case, we can express the efficiency ($\eta$) by [121]:

$$\eta = \frac{I_{\text{exc}}(A)}{I_{\text{exc}}(H)} \cdot \frac{A_H}{A_A} \times 100$$

where $A_A$ and $A_H$ are the measured absorbances at the maxima of A and H respectively and $I_{\text{exc}}(A)$ and $I_{\text{exc}}(H)$ are the excitation intensities at the same wavelengths. This approach has been adopted to estimate excited-state tautomerization in other systems also [122–124].
Figure 11. Theoretical calculations demonstrating ESIPT from higher excited states from reference [118]. Reprinted with permission from (Yuan, H.; Guo, X.; Zhang, J. Ab Initio Insights into the Mechanism of Excited-State Intramolecular Proton Transfer Triggered by the Second Excited Singlet State of a Fluorescent Dye: An anti-Kasha Behavior. Mater. Chem. Front. 2019, 3, 1225–1230. Published by The Royal Society of Chemistry.

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$$\text{Scheme 2. Representative scheme for ground and excited-state tautomerization (A and H represent azo and hydrazone tautomers respectively: $A^*$ and $H^*$ are corresponding excited-state counterparts)} [121] .$$

7. Conclusions and Outlook

In this short review, we have briefly summarized some valuable contributions encompassing critical issues associated with ESIPT. The covered issues are slow and fast ESIPT, effect of hydrogen bonding, substitution and crystal structure (in crystalline phase), ESDPT and its mechanism, excitation wavelength dependence on ESIPT, the role of conical interactions in ESIPT and ground and excited-state tautomerism. We believe the review will provide a platform for furthering efforts in ESIPT from both mechanistic and application points of view.

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References
1. Scheiner, S. Hydrogen Bonding: A Theoretical Perspective; Topics in physical chemistry; Oxford University Press: New York, NY, USA, 1997; ISBN 978-0-19-509011-6.
2. Hynes, J.T.; Klinman, J.P.; Limbach, H.; Schowen, R.L. (Eds.) Hydrogen-Transfer Reactions, 1st ed.; Wiley: Weinheim, Germany, 2006; ISBN 978-3-527-30777-7.
3. Antonov, L. (Ed.) Tautomerism: Methods and Theories; Wiley-VCH: Weinheim, Germany, 2014; ISBN 978-3-527-65884-8.
4. Arnaut, L.G.; Formosinho, S.J. Excited-State Proton Transfer Reactions I. Fundamentals and Intermolecular Reactions. J. Photochem. Photobiol. A Chem. 1993, 75, 1–20. [CrossRef]
5. Formosinho, S.J.; Arnaut, L.G. Excited-State Proton Transfer Reactions II. Intramolecular Reactions. J. Photochem. Photobiol. A Chem. 1993, 75, 21–48. [CrossRef]
6. Ormson, S.M.; Brown, R.G. Excited State Intramolecular Proton Transfer. I: ESIPT to Nitrogen. Prog. React. Kinet. 1994, 19, 45–91.
7. Le Gourrierec, D.; Ormson, S.M.; Brown, R.G. Excited State Intramolecular Proton Transfer. Part 2. ESIPT to Oxygen. Prog. React. Kinet. 1994, 19, 211–275.
8. Douhal, A.; Lahmani, F.; Zewail, A.H. Proton-Transfer Reaction Dynamics. Chem. Phys. 1996, 207, 477–498. [CrossRef]
9. Van der Zwan, G. Dynamics of Ground- and Excited-State Intramolecular Proton Transfer Reactions. In Tautomerism; Antonov, L., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2013; pp. 213–251, ISBN 978-3-527-65882-4.
10. Wu, L.; Han, H.-H.; Liu, L.; Gardiner, J.E.; Sedgwick, A.C.; Huang, C.; Bull, S.D.; He, X.-P.; James, T.D. ESIPT-Based Fluorescence Probe for the Rapid Detection of Peroxynitrite ‘AND’ Biological Thiols. Chem. Commun. 2018, 54, 11336–11339. [CrossRef] [PubMed]
11. Guan, H.; Zhang, A.; Li, P.; Xia, L.; Guo, F. ESIP Fluorescence Probe for Selective and Rapid Detection of Hydrogen Sulfide in Living Cells. ACS Omega 2019, 4, 9113–9119. [CrossRef] [PubMed]

12. Mishra, V.; Misra, V.; Mehta, M.S.; Pant, T.C.; Tripathi, H.B. Fluorescence Studies of Salicylic Acid Doped Poly(Vinyl Alcohol) Film as a Water/Humidity Sensor. J. Phys. Chem. A 2008, 104, 2346–2352. [CrossRef]

13. Chen, L.; Ye, J.-W.; Wang, H.-P.; Pan, M.; Yin, S.-Y.; Wei, Z.-W.; Zhang, L.-Y.; Wu, K.; Fan, Y.-N.; Su, C.-Y. Ultrafast Water Sensing and Thermal Imaging by a Metal-Organic Framework with Switchable Luminescence. Nat. Commun. 2017, 8, 15985. [CrossRef] [PubMed]

14. Misra, V.; Mishra, H. Photoinduced Electron Transfer Coupled with Energy Transfer: Mechanism of Sensitized Luminescence of Terbiyum Ion by Salicylic Acid Doped in Polymer. J. Chem. Phys. 2008, 128, 244701. [CrossRef]

15. Acuña, A.U.; Costela, A.; Munoz, J.M. A Proton-Transfer Laser. J. Phys. Chem. 1986, 90, 2807–2808. [CrossRef]

16. Acuña, A.U.; Correa-Guerrero, P.; Costela, A.; Douhal, A.; Figuera, J.M.; Florido, F.; Sastre, R. Proton-Transfer Lasing from Solid Organic Matrices. Chem. Phys. Lett. 1991, 187, 98–102. [CrossRef]

17. Chou, P.; Mc Morrow, D.; Aartsma, T.J.; Kashka, M. The Proton-Transfer Laser. Gain Spectrum and Amplification of Spontaneous Emission of 3-Hydroxylflavone. J. Phys. Chem. 1984, 88, 4596–4599. [CrossRef]

18. Yan, C.-C.; Wang, X.-D.; Liao, L.-S. Organic Lasers Harnessing Excited State Intramolecular Proton Transfer Process. ACS Photonics 2020, 7, 1355–1366. [CrossRef]

19. Tsutsui, Y.; Zhang, W.; Ghosh, S.; Sakurai, T.; Yoshida, H.; Ozaki, M.; Akutagawa, T.; Seki, S. Electrically Switchable Amplified Spontaneous Emission from Liquid Crystalline Phase of an AIEE-Active ESIP Molecule. Adv. Opt. Mater. 2020, 8, 1902158. [CrossRef]

20. Catalan, J.; Fabero, F.; Soledad Guijarro, M.; Claramunt, R.M.; Santa Maria, M.D.; de la Foces-Foces, M.C.; Hernandez Cano, F.; Elguero, J.; Sastre, R. Photoinduced Intramolecular Proton Transfer as the Mechanism of Ultraviolet Stabilizers: A Reappraisal. J. Am. Chem. Soc. 1990, 112, 747–759. [CrossRef]

21. Long, Y.; Mamada, M.; Li, C.; dos Santos, P.L.; Colella, M.; Danos, A.; Adachi, C.; Monkman, A. Exited State Dynamics of Thermally Activated Delayed Fluorescence from an Excited State Intramolecular Proton Transfer System. J. Phys. Chem. Lett. 2020, 11, 3305–3312. [CrossRef] [PubMed]

22. Jiang, G.; Li, F.; Fan, J.; Song, Y.; Wang, C.-K.; Lin, L. Theoretical Perspective for Luminescent Mechanism of Thermally Activated Delayed Fluorescence Emitter with Excited-State Intramolecular Proton Transfer. J. Mater. Chem. C 2020, 8, 98–108. [CrossRef]

23. Tang, K.-C.; Chang, M.-J.; Lin, T.-Y.; Pan, H.-A.; Fang, T.-C.; Chen, K.-Y.; Hung, W.-Y.; Hsu, Y.-H.; Chou, P.-T. Fine Tuning the Energetics of Excited-State Intramolecular Proton Transfer (ESIPT): White Light Generation in a Single ESIPT System. J. Am. Chem. Soc. 2011, 133, 17738–17747. [CrossRef]

24. Moraes, E.S.; Teixeira Alves Duarte, L.G.; Germino, J.C.; Atvars, T.D.Z. Near Attack Conformation as Strategy for ESIPT Modulation for White-Light Generation. J. Phys. Chem. C 2020, 124, 22406–22415. [CrossRef]

25. Serdiuk, I.E. Design and Emissive Features of Ionic White-Light Fluorophore. J. Phys. Chem. C 2018, 122, 18615–18620. [CrossRef]

26. Zhang, Z.; Chen, Y.-A.; Hung, W.-Y.; Tang, W.-F.; Hsu, Y.-H.; Chen, C.-L.; Meng, F.-Y.; Chou, P.-T. Control of the Reversibility of Excited-State Intramolecular Proton Transfer (ESIPT) Reaction: Host-Polarity Tuning White Organic Light Emitting Diode on a New Thiazolo[5,4-d]Thiazole ESIPT System. Chem. Mater. 2016, 28, 8815–8824. [CrossRef]

27. Sedgwick, A.C.; Wu, L.; Han, H.-H.; Bull, S.D.; He, X.-P.; James, T.D.; Sessler, J.L.; Tang, B.Z.; Tian, H.; Yoon, J. Excited-State Intramolecular Proton-Transfer (ESIPT) Based Fluorescence Sensors and Imaging Agents. Chem. Soc. Rev. 2018, 47, 8842–8880. [CrossRef]

28. Wu, Y.; Peng, X.; Fan, J.; Gao, S.; Tian, M.; Zhao, J.; Sun, S. Fluorescence Sensing of Anions Based on Inhibition of Excited-State Intramolecular Proton Transfer. J. Org. Chem. 2007, 72, 62–70. [CrossRef]

29. Zhang, X.; Guo, L.; Wu, F.-Y.; Jiang, Y.-B. Development of Fluorescent Sensing of Anions under Excited-State Intramolecular Proton Transfer Signaling Mechanism. Org. Lett. 2003, 5, 2667–2670. [CrossRef] [PubMed]

30. Henary, M.M.; Wu, Y.; Fahimi, C.J. Zinc(II)-Selective Ratiometric Fluorescent Sensors Based on Inhibition of Excited-State Intramolecular Proton Transfer. Chem. Eur. J. 2004, 10, 3015–3025. [CrossRef] [PubMed]

31. Lim, S.-J.; Seo, J.; Park, S.Y. Photochromic Switching of Excited-State Intramolecular Proton-Transfer (ESIPT) Fluorescence: A Unique Route to High-Contrast Memory Switching and Nondestructive Readout. J. Am. Chem. Soc. 2006, 128, 14542–14547. [CrossRef]

32. Sobolewski, A.L. Reversible Molecular Switch Driven by Excited-State Hydrogen Transfer. Phys. Chem. Chem. Phys. 2008, 10, 1243. [CrossRef]

33. Berenbeim, J.A.; Boldissar, S.; Owens, S.; Haggmark, M.R.; Gate, G.; Siouri, F.M.; Cohen, T.; Rode, M.F.; Patterson, C.S.; de Vries, M.S. Excited State Intramolecular Proton Transfer in Hydroxanthraquinones: Toward Predicting Predicting of Organic Red Colorants in Art. Sci. Adv. 2019, 5, eaaw5227. [CrossRef] [PubMed]

34. Weller, A. Über die Fluoreszenz der Salizylsäure und verwandter Verbindungen. Naturwissenschaften 1955, 42, 175–176. [CrossRef]

35. Weller, A. Intramolekularer Protonenübergang Im Angeregten Zustand. Z. Für Elektrochem. Ber. Der Bunsenges. Für Phys. Chem. 1956, 60, 1144–1147. [CrossRef]

36. Waluk, J. Proton or Hydrogen Transfer? Charge Distribution Analysis. Pol. J. Chem. 2008, 82, 947–962.
37. Konijnenberg, J.; Ekelmans, G.B.; Huizier, A.H.; Varma, C.A.G.O. Mechanism and Solvent Dependence of the Solvent-Catalysed Pseudo-Intramolecular Proton Transfer of 7-Hydroxyquinoline in the First Electronically Excited Singlet State and in the Ground State of Its Tautomer. J. Chem. Soc. Faraday Trans. 2 1989, 85, 39–51. [CrossRef]

38. Sandros, K.; Seip, R.; Østvold, T.; Pohjonen, M.-L.; Koski, J. Hydrogen Bonding Effects on the Fluorescence of Methyl Salicylate. Acta Chem. Scand. 1976, 30a, 761–763. [CrossRef]

39. Kovi, P.; Miller, C.L.; Schulman, S.G. Biprotonic versus Intramolecular Phototautomerism of Salicylic Acid and Some of Its Methylated Derivatives in the Lowest Excited Singlet State. Anal. Chim. Acta 1972, 61, 7–13. [CrossRef]

40. Smith, K.K.; Kaufmann, K.J. Solvent Dependence of the Nonradiative Decay Rate of Methyl Salicylate. J. Phys. Chem. 1981, 85, 2895–2897. [CrossRef]

41. Heimbrook, L.; Kenny, J.E.; Kohler, B.E.; Scott, G.W. Lowest Excited Singlet State of Hydrogen-Bonded Methyl Salicylate. J. Phys. Chem. 1983, 87, 280–289. [CrossRef]

42. Herek, J.L.; Pedersen, S.; Bañares, L.; Zewail, A.H. Femtosecond Real-time Probing of Reactions. IX. Hydrogen-atom Transfer. J. Chem. Phys. 1992, 97, 9046–9061. [CrossRef]

43. Toribio, F.; Catalan, J.; Amat, F.; Acuna, A.U. Electronically Induced Proton-Transfer Reactions in Salicylic Acid Esters and Salicyloyl Chloride. J. Phys. Chem. 1983, 87, 817–822. [CrossRef]

44. Kosower, E.M.; Dodiuk, H. Multiple Fluororescences III. Methyl 2,6-Dihydroxybenzoate and Methyl Salicylate. J. Lumin. 1975, 11, 249–254. [CrossRef]

45. Acuna, A.U.; Amat-Guerrí, F.; Catalan, J.; Gonzalez-Tablas, F. Dual Fluorescence and Ground State Equilibria in Methyl Salicylate, Methyl 3-Chlorosalicylate, and Methyl 3-Tert-Butylsalicylate. J. Phys. Chem. 1980, 84, 629–631. [CrossRef]

46. Pant, D.D.; Joshi, H.C.; Bisht, P.B.; Tripathi, H.B. Dual Emission and Double Proton Transfer in Salicylic Acid. Chem. Phys. 1994, 185, 137–144. [CrossRef]

47. Denisov, G.S.; Golubev, N.S.; Schreiber, V.M.; Shahakmedov, S.S.; Shurukhina, A.V. Excited State Intramolecular Proton Transfer and Dual Emission of the Cyclic Homo- and Heterodimers of 2-Hydroxy- and 2,6-Dihydroxy Benzoic Acids. J. Mol. Struct. 1996, 381, 73–81. [CrossRef]

48. Young, J.W.; Fleisher, A.J.; Pratt, D.W. Exploring Single and Double Proton Transfer Processes in the Gas Phase: A High Resolution Electronic Spectroscopy Study of 5-Fluorosalicylic Acid. J. Chem. Phys. 2011, 134, 084310. [CrossRef] [PubMed]

49. Wu, C.-H.; Karas, L.J.; Ottosson, H.; Wu, J.I.-C. Excited-State Proton Transfer Relieves Antiaromaticity in Molecules. Proc Natl Acad. Sci. USA 2019, 116, 20303–20308. [CrossRef] [PubMed]

50. Bisht, P.B.; Petek, H.; Yoshii, K.; Nagashima, U. Excited State Eno1-keto Tautomerization in Salicylic Acid: A Supersonic Free Jet Study. J. Chem. Phys. 1995, 103, 5290–5307. [CrossRef]

51. Joshi, H.C.; Tripathi, H.B.; Pant, T.C.; Pant, D.D. Hydrogen-Bonding Effect on the Dual Emission of Salicylic Acid. Chem. Phys. Lett. 1990, 173, 83–86. [CrossRef]

52. Denisov, G.S.; Golubev, N.S.; Schreiber, V.M.; Shahakmedov, S.S.; Shurukhina, A.V. Effect of Intermolecular Hydrogen Bonding and Proton Transfer on Fluorescence of Salicylic Acid. J. Mol. Struct. 1997, 436–437, 153–160. [CrossRef]

53. Joshi, H.C.; Mishra, H.; Tripathi, H.B. Photophysics and Photochemistry of Salicylic Acid Revisited. J. Photochem. Photobiol. A Chem. 1997, 105, 15–20. [CrossRef]

54. Lahmani, F.; Zehacker-Rentien, A. Effect of Substitution on the Photoinduced Intramolecular Proton Transfer in Salicylic Acid. J. Phys. Chem. A 1997, 101, 6141–6147. [CrossRef]

55. Smoluch, M.; Joshi, H.; Gerssen, A.; Goosje, C.; van der Zwan, G. Fast Excited-State Intramolecular Proton Transfer and Subnanosecond Dynamic Stokes Shift of Time-Resolved Fluorescence Spectra of the 5-Methoxysalicylic Acid/Diethyl Ether Complex. J. Phys. Chem. A 2005, 109, 535–541. [CrossRef]

56. Acuña, A.U.; Toribio, F.; Amat-Guerrí, F.; Catalán, J. Excited State Proton Transfer: A New Feature in the Fluorescence of Methyl 5-Chlorosalicylate and Methyl 5-Methoxysalicylate. J. Photochem. 1985, 30, 339–352. [CrossRef]

57. Abd El-Hakam Abou El-Nasr, E.; Fujii, A.; Ebata, T.; Mikami, N. Substitution Effects on the Excited-State Intramolecular Proton Transfer of Salicylic Acid: An Infrared Spectroscopic Study on the OH Stretching Vibrations of Jet-Cooled 5-Methoxysalicylic Acid. Chem. Phys. Lett. 2003, 376, 788–793. [CrossRef]

58. Maheshwary, S.; Lourderaj, U.; Sathyamurthy, N. Ab Initio Quantum Chemical Investigation of the Ground and Excited States of Salicylic Acid Dimer. J. Phys. Chem. A 2006, 110, 12662–12669. [CrossRef]

59. Sobolewski, A.L.; Domcke, W. Ab Initio Potential-Energy Functions for Excited State Intramolecular Proton Transfer: A Comparative Study of o-Hydroxybenzaldehyde, Salicylic Acid and 7-Hydroxy-1-Indanone. Phys. Chem. Chem. Phys. 1999, 1, 3065–3072. [CrossRef]

60. Sobolewski, A.L.; Domcke, W. Photophysics of Intramolecularly Hydrogen-Bonded Aromatic Systems: Ab Initio Exploration of the Excited-State Deactivation Mechanisms of Salicylic Acid. Phys. Chem. Chem. Phys. 2006, 8, 3410. [CrossRef]

61. Yahagi, T.; Fujii, A.; Ebata, T.; Mikami, N. Infrared Spectroscopy of the OH Stretching Vibrations of Jet-Cooled Salicylic Acid and Its Dimer in S0 and S1. J. Phys. Chem. A 2001, 105, 10673–10680. [CrossRef]

62. Morsi, S.E.; Williams, J.O. Fluorescence and Reactivity of P-Aminosalicylic Acid: An Example of Proton Transfer in the Solid State. J. Chem. Soc. Perkin Trans. 2 1978, 1280. [CrossRef]
63. Maheshwari, S.; Chowdhury, A.; Sathyamurthy, N.; Mishra, H.; Tripathi, H.B.; Panda, M.; Chandrasekhar, J. Ground and Excited State Intramolecular Proton Transfer in Salicylic Acid: An Ab Initio Electronic Structure Investigation. *J. Phys. Chem. A* 1999, 103, 6257–6262. [CrossRef]

64. Friedrich, D.M.; Wang, Z.; Joly, A.G.; Peterson, K.A.; Callis, P.R. Ground-State Proton-Transfer Tautomer of the Salicylate Anion. *J. Phys. Chem. A* 1999, 103, 9644–9653. [CrossRef]

65. Joshi, H.C.; Gooijer, C.; van der Zwan, G. Water-Induced Quenching of Salicylic Anion Fluorescence. *J. Phys. Chem. A* 2002, 106, 11422–11430. [CrossRef]

66. Joshi, H.C.; Gooijer, C.; van der Zwan, G. Substitution Effects on the Photophysical Characteristics of the Salicylic Anion. *J. Fluoresc.* 2003, 13, 227–234. [CrossRef]

67. Tiwari, A.K.; Sathyamurthy, N. Structure and Stability of Salicylic Acid–Water Complexes and the Effect of Molecular Hydration on the Spectral Properties of Salicylic Acid. *J. Phys. Chem. A* 2006, 110, 5960–5964. [CrossRef]

68. Vener, M.V.; Scheiner, S. Hydrogen Bonding and Proton Transfer in the Ground and Lowest Excited Singlet States of O-Hydroxyacetophenone. *J. Phys. Chem. A* 1995, 99, 642–649. [CrossRef]

69. Sobolewski, A.L.; Domcke, W. Ab Initio Study of Excited-State Intramolecular Proton Dislocation in Salicylic Acid. *Chem. Phys.* 1998, 232, 257–265. [CrossRef]

70. Jang, Sungwoo; Jin, Sung Il; Park, Chan Ryang TDDFT Potential Energy Functions for Excited State Intramolecular Proton Transfer of Salicylic Acid, 3-Aminosalicylic Acid, 5-Aminosalicylic Acid, and 5-Methoxysalicylic Acid. *Bull. Korean Chem. Soc.* 2007, 28, 2343–2353. [CrossRef]

71. Adhikari, M.; Joshi, N.K.; Joshi, H.C.; Mehta, M.S.; Mishra, H.; Pant, S. Revisiting the Photochemistry 2,5-dihydroxy Benzoic Acid (Genticis Acid): Solvent and PH Effect. *J. Phys. Org. Chem.* 2020. [CrossRef]

72. Wolfe, G.J.; Thistlethwaite, P.J. Excited-State Prototropism in Esters of o-Hydroxy-2-Naphthoic Acids. *J. Am. Chem. Soc.* 1981, 103, 3849–3854. [CrossRef]

73. Catalán, J.; del Valle, J.C.; Palomar, J.; Diaz, C.; de Paz, J.L.G. The Six-Membered Intramolecular Hydrogen Bond Position as a Switch for Inducing an Excited State Intramolecular Proton Transfer (ESIPT) in Esters of o-Hydroxynaphthoic Acids. *J. Phys. Chem. A* 1999, 103, 10921–10934. [CrossRef]

74. Mishra, H.; Joshi, H.C.; Tripathi, H.B.; Maheshwary, S.; Sathyamurthy, N.; Panda, M.; Chandrasekhar, J. Photoinduced Proton Transfer in 3-Hydroxy-2-Naphthoic Acid. *J. Photochem. Photobiol. A Chem.* 2001, 139, 23–36. [CrossRef]

75. Mishra, H.; Maheshwary, S.; Tripathi, H.B.; Sathyamurthy, N. An Experimental and Theoretical Investigation of the Photophysics of 1-Hydroxy-2-Naphthoic Acid. *J. Phys. Chem. A* 2005, 109, 2746–2754. [CrossRef]

76. Mishra, H. Photo-Induced Relaxation and Proton Transfer in Some Hydroxy Naphthoic Acids in Polymers. *J. Phys. Chem. B* 2006, 110, 9387–9396. [CrossRef]

77. Southern, C.A.; Levy, D.H.; Florio, G.M.; Longarte, A.; Zwier, T.S. Electronic and Infrared Spectroscopy of Anthranilic Acid in a Supersonic Jet. *J. Phys. Chem. A* 2003, 107, 4032–4040. [CrossRef]

78. Southern, C.A.; Levy, D.H.; Stearns, J.A.; Florio, G.M.; Longarte, A.; Zwier, T.S. Spectroscopic Consequences of Localized Electronic Excitation in Anthranilic Acid Dimer. *J. Phys. Chem. A* 2004, 108, 4599–4609. [CrossRef]

79. Stearns, J.A.; Das, A.; Zwier, T.S. Hydrogen Atom Dislocation in the Excited State of Anthranilic Acid: Probing the Carbonyl Stretch Fundamental and the Effects of Water Complexation. *Phys. Chem. Chem. Phys.* 2004, 6, 2605. [CrossRef]

80. Blodgett, K.N.; Sun, D.; Fischer, J.L.; Sibert, E.L.; Zwier, T.S. Vibration Spectroscopy of Methyl Anthranilate and Its Water Complex: Hydrogen Atom Dislocation in the Excited State. *Phys. Chem. Chem. Phys.* 2019, 21, 21355–21369. [PubMed]

81. Blodgett, K.N.; Fischer, J.L.; Zwier, T.S.; Sibert, E.L. The Missing NH Stretch Fundamental in S1 Methyl Anthranilate: IR-UV Double Resonance Experiments and Local Mode Theory. *Phys. Chem. Chem. Phys.* 2020, 22, 14077–14087. [CrossRef]

82. Kolek, P.; Andrezejak, M.; Uchacz, T.; Szlachcic, P. Consistent Franck–Condon Modeling of Geometry Changes for the S0→S1(1πt) Excitation in Anthranilic Acid: LIF Spectroscopy Aided by CC2 or TDDFT Vibrations. *J. Quant. Spectrosc. Radiat. Transf.* 2020, 242, 106747. [CrossRef]

83. Bader, A.N.; Ariere, F.; Gooijer, C. Proton Transfer in 3-Hydroxyflavone Studied by High-Resolution 10 K Laser-Excited Shpol’skii Spectroscopy. *J. Phys. Chem. A* 2002, 106, 2844–2849. [CrossRef]

84. Ameer-Beg, S.; Ormsom, S.M.; Brown, R.G.; Matousek, P.; Towie, M.; Nibbering, E.T.J.; Foggi, P.; Neuwahl, F.V.R. Ultrafast Measurements of Excited State Intramolecular Proton Transfer (ESIPT) in Room Temperature Solutions of 3-Hydroxyflavone and Derivatives. *J. Phys. Chem. A* 2001, 105, 3709–3718. [CrossRef]

85. Furukawa, K.; Yamamoto, N.; Hino, K.; Sekiya, H. Excited-State Intramolecular Proton Transfer and Conformational Relaxation in 4′-N,N-Dimethylamino-3-Hydroxyflavone Doped in Acantharil Crystals. *Phys. Chem. Chem. Phys.* 2016, 18, 28564–28575. [CrossRef]

86. Zamotaiev, O.M.; Shvadchak, V.; Sych, T.P.; Melnychuk, N.A.; Yuschenko, D.; Mely, Y.; Pivovarenko, V.G. Environment-Sensitive Quinolone Demonstrating Long-Lived Fluorescence and Unusually Slow Excited-State Intramolecular Proton Transfer Kinetics. *Methods Appl. Fluoresc.* 2016, 4, 034004. [CrossRef]

87. Hristova, S.; Dobrikov, G.; Kamounah, F.S.; Kawauchi, S.; Hansen, P.E.; Deneva, V.; Nedeltcheva, D.; Antonov, L. 10-Hydroxybenzo[h]Quinoline: Switching between Single- and Double-Well Proton Transfer through Structural Modifications. *RSC Adv.* 2015, 5, 102495–102507. [CrossRef]
88. Marciniak, H.; Hristova, S.; Deneva, V.; Kamounah, F.S.; Hansen, P.E.; Lochbrunner, S.; Antonov, L. Dynamics of Excited State Proton Transfer in Nitro Substituted 10-Hydroxybenzo[h]Quinolines. *Phys. Chem. Chem. Phys.* 2017, 19, 26621–26629. [CrossRef]

89. Joshi, N.K.; Arora, P.; Pant, S.; Joshi, H.C. Slow Excited State Phototautomerization in 3-Hydroxyisoquinoline. *Photochem. Photobiol. Sci.* 2014, 13, 929. [CrossRef] [PubMed]

90. Kuang, Z.; Guo, Q.; Wang, X.; Song, H.; Maroncelli, M.; Xia, A. Ultrafast Ground-State Intramolecular Proton Transfer in Diethylaminohydroxylflavone Resolved with Pump–Dump–Probe Spectroscopy. *J. Phys. Chem. Lett.* 2018, 9, 4174–4181. [CrossRef] [PubMed]

91. Yushchenko, D.A.; Shvadchak, V.V.; Klymchenko, A.S.; Duportail, G.; Pivovarenko, V.G.; Mely, Y. Steric Control of the Excited-State Intramolecular Proton Transfer in 3-Hydroxyquinolines: Steady-State and Time-Resolved Fluorescence Study. *J. Phys. Chem. A* 2007, 111, 8896–8992. [CrossRef] [PubMed]

92. Liu, Z.-Y.; Hu, J.-W.; Huang, T.-H.; Chen, K.-Y.; Chou, P.-T. Excited-State Intramolecular Proton Transfer in the Kinetic-Control Regime. *Phys. Chem. Chem. Phys.* 2020, 22, 22271–22278. [CrossRef]

93. Khimich, M.N.; Ivanov, V.L.; Melnikov, M.Y.; Shelaev, I.V.; Gostev, E.E.; Nadtochenko, V.A.; Uzhinov, B.M. Dynamics of Excited-State Intramolecular Proton-Transfer in 2-Amino-3-(Z-Benzazolyl)Quinoline Cations. *Photochem. Photobiol. Sci.* 2017, 16, 1139–1145. [CrossRef]

94. Perveaux, A.; Lorphein, A.; Lasorne, B.; Lauvergnat, D. Fast and Slow Excited-State Intramolecular Proton Transfer in 3-Hydroxychromone: A Two-State Story? *Phys. Chem. Chem. Phys.* 2017, 19, 6579–6593. [CrossRef]

95. Ray, D.; Pramanik, A.; Guchhait, N. Slow Excited-State Proton Transfer Dynamics of a Four Member Intramolecular Hydrogen Bonded Isoindole Fused Imidazole System: A Spectroscopic Approach to Photophysical Properties. *J. Photochem. Photobiol. A: Chem.* 2015, 302, 42–50. [CrossRef]

96. Zhang, N.; Liu, D.; Chen, W.; Liu, X.; Yan, J. Solvent Effect on Excited-State Intramolecular Proton Transfer Process Based on ‘Naked’ Diazaborepins. *Comput. Theor. Chem.* 2020, 1185, 112898. [CrossRef]

97. Ni, M.; Su, S.; Fang, H. Substituent Control of Photophysical Properties for Excited-State Intramolecular Proton Transfer (ESIPT) of o-LHBDI Derivatives: A TD-DFT Investigation. *J. Mol. Model.* 2020, 26, 108. [CrossRef]

98. Park, S.-Y.; Kim, B.; Lee, Y.-S.; Kwon, O.-H.; Jang, D.-J. Triple Proton Transfer of Excited 7-Hydroxyquinoline along a Hydrogen-Bonded Water Chain in Ethers: Secondary Solvent Effect on the Reaction Rate. *Photochem. Photobiol. Sci.* 2009, 8, 1611. [CrossRef] [PubMed]

99. Mehata, M.S.; Joshi, H.C.; Tripathi, H.B. Excited-State Intramolecular Proton Transfer Reaction of 6-Hydroxyquinoline in Protic Polar Medium. *Chem. Phys. Lett.* 2002, 354, 314–320. [CrossRef]

100. Jang, H.-J.; Schrieber, C.; Barbatti, M.; Stock, K.; Aquino, A.J.A.; Tunega, D.; Lochbrunner, S.; Riedle, E.; de Vivie-Riedle, R.; Lischka, H. The Interplay of Skeletal Deformations and Ultrafast Excited-State Intramolecular Proton Transfer: Experimental and Theoretical Investigation of 10-Hydroxybenzo[h]Quinoline. *Chem. Phys.* 2008, 347, 446–461. [CrossRef]

101. Mehata, M.S. Photoinduced Excited State Proton Rearrangement of 6-Hydroxyquinoline along a Hydrogen-Bonded Acetic Acid Wire. *Chem. Phys. Lett.* 2007, 436, 357–361. [CrossRef]

102. Liu, Y.-H.; Mehata, M.S.; Liu, J.-Y. Excited-State Proton Transfer via Hydrogen-Bonded Acetic Acid (AcOH) Wire for 6-Hydroxyquinoline. *J. Phys. Chem. A* 2011, 115, 19–24. [CrossRef]

103. Park, S.-Y.; Kim, B.; Lee, Y.-S.; Kwon, O.-H.; Jang, D.-J. Triple Proton Transfer of Excited 7-Hydroxyquinoline along a Hydrogen-Bonded Water Chain in Ethers: Secondary Solvent Effect on the Reaction Rate. *Photochem. Photobiol. Sci.* 2009, 8, 1611. [CrossRef] [PubMed]

104. Kim, Y.-J.; Kwon, O.-H. Proton Diffusion Dynamics along a Diol as a Proton-Conducting Wire in a Photo-Amphiprotic Model System. *Phys. Chem. Chem. Phys.* 2016, 18, 32826–32839. [CrossRef] [PubMed]

105. Alarcos, N.; Gutierrez, M.; Liras, M.; Sánchez, F.; Douhal, A. An Abnormally Slow Proton Transfer Reaction in a Simple HBO Derivative Due to Ultrafast Intramolecular-Charge Transfer Events. *Phys. Chem. Chem. Phys.* 2015, 17, 16257–16269. [CrossRef]

106. Dommett, M.; Rivera, M.; Smith, M.T.H.; Crespo-Otero, R. Molecular and Crystalline Requirements for Solid State Fluorescence Exploiting Excited State Intramolecular Proton Transfer. *J. Mater. Chem. C* 2020, 8, 2558–2568. [CrossRef]

107. Taylor, C.A.; El-Bayoumi, M.A.; Kashar, M. Excited-State Tow-Photon Tautomerism in Hydrogen Bonded NHeterocyclic Base Pairs. *Proc. Natl. Acad. Sci. USA* 1969, 63, 253–260. [CrossRef] [PubMed]

108. Ingham, K.C.; Abu-Elgheit, M.; El-Bayoumi, M.A. Confirmation of Biprotonic Phototautomerism in 7-Azaindole Hydrogen-Bonded Dimers. *J. Am. Chem. Soc.* 1971, 93, 5023–5025. [CrossRef]

109. Hetherington, W.M.; Micheels, R.H.; Eisenholt, K.E. Picosecond Dynamics of Double Proton Transfer in 7-Azaindole Dimers. *Chem. Phys. Lett.* 1979, 66, 230–233. [CrossRef]

110. Douhal, A.; Kim, S.K.; Zewail, A.H. Femtosecond Molecular Dynamics of Tautomerization in Model Base Pairs. *Nature* 1995, 378, 260–263. [CrossRef] [PubMed]

111. Kwon, O.-H.; Zewail, A.H. Double Proton Transfer Dynamics of Model DNA Base Pairs in the Condensed Phase. *Proc. Natl. Acad. Sci. USA* 2007, 104, 8703–8708. [CrossRef] [PubMed]

112. Feldmar, D.E.; Wisniewski, E.S.; Hurley, S.M.; Castleman, A.W. Femtosecond Cluster Studies of the Solvated 7-Azaindole Excited State Double-Proton Transfer. *Proc. Natl. Acad. Sci. USA* 1999, 96, 12980–12986. [CrossRef] [PubMed]

113. Takeuchi, S.; Tahara, T. The Answer to Concerted versus Step-Wise Controversy for the Double Proton Transfer Mechanism of 7-Azaindole Dimer in Solution. *Proc. Natl. Acad. Sci. USA* 2007, 104, 5285–5290. [CrossRef]
114. Crespo-Otero, R.; Kungwan, N.; Barbatti, M. Stepwise Double Excited-State Proton Transfer Is Not Possible in 7-Azaindole Dimer. *Chem. Sci.* **2015**, *6*, 5762–5767. [CrossRef] [PubMed]

115. Zhou, P.; Han, K. Unraveling the Detailed Mechanism of Excited-State Proton Transfer. *Acc. Chem. Res.* **2018**, *51*, 1681–1690. [CrossRef]

116. Demchenko, A.P.; Tomin, V.I.; Chou, P.-T. Breaking the Kasha Rule for More Efficient Photochemistry. *Chem. Rev.* **2017**, *117*, 13353–13381. [CrossRef]

117. Tseng, H.-W.; Shen, J.-Y.; Kuo, T.-S.; Chen, Y.-A.; Demchenko, A.P.; Chou, P.-T. Excited-State Intramolecular Proton-Transfer Reaction Demonstrating Anti-Kasha Behavior. *Chem. Sci.* **2016**, *7*, 655–665. [CrossRef]

118. Yuan, H.; Guo, X.; Zhang, J. *Ab Initio* Insights into the Mechanism of Excited-State Intramolecular Proton Transfer Triggered by the Second Excited Singlet State of a Fluorescent Dye: An Anti-Kasha Behavior. *Mater. Chem. Front.* **2019**, *3*, 1225–1230. [CrossRef]

119. Del Valle, J.C.; Catalán, J. Kasha’s Rule: A Reappraisal. *Phys. Chem. Chem. Phys.* **2019**, *21*, 10061–10069. [CrossRef] [PubMed]

120. Jacques, P. Solvent Effects on the Photochemical Behaviour of 4-Phenylazo-1-Naphthol: A Flash Photolysis Study. *Dye. Pigment.* **1988**, *9*, 129–135. [CrossRef]

121. Joshi, H.; Kamounah, F.S.; Gooijer, C.; van der Zwan, G.; Antonov, L. Excited State Intramolecular Proton Transfer in Some Tautomeric Azo Dyes and Schiff Bases Containing an Intramolecular Hydrogen Bond. *J. Photochem. Photobiol. A Chem.* **2002**, *152*, 183–191. [CrossRef]

122. Yordanov, D.; Deneva, V.; Georgiev, A.; Crochet, A.; Fromm, K.M.; Antonov, L. Indirect Solvent Assisted Tautomerism in 4-Substituted Phthalimide 2-Hydroxy-Schiff Bases. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2020**, *237*, 118416. [CrossRef] [PubMed]

123. Georgiev, A.; Todorov, P.; Dimov, D. Excited State Proton Transfer and E/Z Photoswitching Performance of 2-Hydroxy-1-Naphthalene and 1-Naphthalene 5,5′-Dimethyl- and 5,5′-Diphenylhydantoin Schiff Bases. *J. Photochem. Photobiol. A Chem.* **2020**, *386*, 112143. [CrossRef]

124. Todorov, P.; Georgieva, S.; Peneva, P.; Rusew, R.; Shivachev, B.; Georgiev, A. Experimental and Theoretical Study of Bidirectional Photoswitching Behavior of 5,5′-Diphenylhydantoin Schiff Bases: Synthesis, Crystal Structure and Kinetic Approaches. *New J. Chem.* **2020**, *44*, 15081–15099. [CrossRef]

125. Wnuk, P.; Burdzielinski, G.; Sliwa, M.; Kijak, M.; Grabowska, A.; Sepioł, J.; Kubicki, J. From Ultrafast Events to Equilibrium – Uncovering the Unusual Dynamics of ESIPT Reaction: The Case of Dually Fluorescent Diethyl-2,5-(Dibenzoxazolyl)-Hydroquinone. *Phys. Chem. Chem. Phys.* **2014**, *16*, 2542. [CrossRef]

126. Ma, Y.; Yang, Y.; Lan, R.; Li, Y. Effect of Different Substituted Groups on Excited-State Intramolecular Proton Transfer of 1-(Acylamino)-Anthraquinons. *J. Phys. Chem. C* **2017**, *121*, 14779–14786. [CrossRef]

127. Kyrchenko, A.; Herlich, J.; Waluk, J. Studies of Photoinduced NH Tautomerism by Stationary and Time-Resolved Fluorescence Techniques. In *Tautomerism*; Antonov, L., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2013; pp. 49–78, ISBN 978-3-527-65882-4.

128. Zhao, J.; Chen, J.; Liu, X.; Zheng, Y. Controlling Excited State Single versus Double Proton Transfer for 2,2′-Bipyridyl-3,3′-Diol: Solvent Effect. *J. Phys. Chem. A* **2017**, *121*, 4002–4008. [CrossRef]

129. Plasser, F.; Barbatti, M.; Aquino, A.J.A.; Lischka, H. Excited-State Diproton Transfer in [2,2′-Bipyridyl]-3,3′-Diol: The Mechanism Is Sequential, Not Concerted. *J. Phys. Chem. A* **2009**, *113*, 8490–8499. [CrossRef]

130. Savarese, M.; Brémond, É.; Antonov, L.; Ciofini, I.; Adamo, C. Computational Insights into Excited-State Proton-Transfer Reactions in Azo and Azomethine Dyes. *ChemPhysChem* **2015**, *16*, 3966–3973. [CrossRef] [PubMed]