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Spectroscopic and semi-empirical MO study of substituent effects on the intramolecular proton transfer in anils of 2-hydroxybenzaldehydes

Sergio H. Alarcón[a], Daniela Pagani[a], José Bacigalupo[b], Alejandro C. Olivieri[a,*]

[a]*Departamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531, Rosario 2000, Argentina*

[b]*IQUIOS, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531, Rosario 2000, Argentina*

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Abstract

Substituent effects in singly and doubly substituted anils of 2-hydroxybenzaldehyde showing strong intramolecular hydrogen bonding are studied on the basis of solution ^{13}C NMR spectroscopic data and semiempirical MO (AM1) calculations of the relative stability of tautomers. Excited state proton transfer is also investigated using electronic absorption and fluorescence spectroscopies, and calculation of vertical excitation energies (INDO/S). The theoretical predictions are in agreement with the experimental observations.

Keywords: Proton transfer; Substituent effects; Spectroscopy and MO calculations; Anils of 2-hydroxybenzaldehyde

1. Introduction

Hydrogen bonded systems, both in solution and in the solid phase, have attracted considerable attention over the years [1–4]. Especially interesting are those structures where one or more hydrogens are transferred with an accompanying tautomeric change [5–14]. A knowledge of these processes is fundamental not only to the understanding of the chemical behaviour of these interesting systems, but could convey technological implications, as proton exchanging materials can be utilized for designing molecular electronic devices [15–19].

A prototropic tautomeric behaviour has been recognized in a number of aromatic Schiff bases [20–38]. *N*-Salicylideneaniline derivatives are known to show a self-isomerization induced by an intramolecular proton transfer from the hydroxyl oxygen to the imine nitrogen through the O–H$^{\bullet\bullet\bullet}$N hydrogen bond (Scheme 1) [35–38]. In our preceding reports we characterized the structures of several anils of aromatic α-hydroxyaldehydes (salicylaldehyde, 2-hydroxynaphthalene-1-carbaldehyde and 10-hydroxy phenanthrene-9-carbaldehyde), all of which display both ground and excited state proton transfer processes in solution, as well as in the solid state [35–38]. From NMR spectral data, it has been confirmed that these compounds exist as an equilibrium mixture of the enol-imine form **a** and the keto-enamine form **b** (Scheme 1). In *p*-substituted anils of 2-hydroxybenzaldehyde and 10-hydroxyphenanthrene-9-carbaldehyde, the dominant forms are **a** and **b**, respectively, whereas in the case of anils of

* Corresponding author. Tel.: +00-54-41-372704; Fax: +00-54-41-372704; E-mail: aolivier@fbioyf.unr.edu.ar

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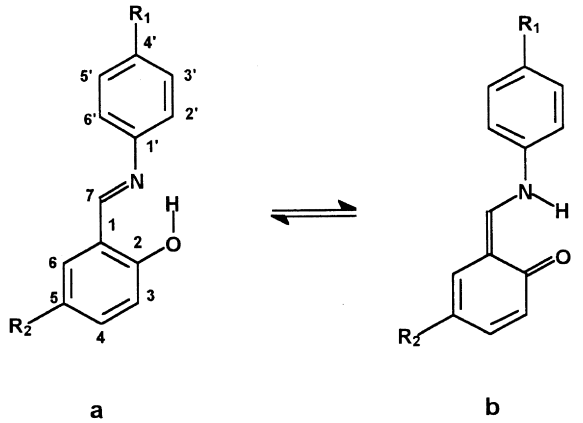


	R_1	R_2
1	NO_2	NO_2
2	H	NO_2
3	MeO	NO_2
4	NO_2	H
5	H	H
6	MeO	H
7	NO_2	MeO
8	H	MeO
9	MeO	MeO

Scheme 1. Structures of studied compounds.

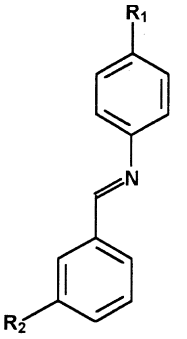
2-hydroxynaphthalene-1-carbaldehyde an equilibrium exists with significant amounts of both forms [35,37]. Contrasting the structurally related α-hydroxy-arylazo systems, where substituent effects at C4′ strongly influence the position of the enol-azo/keto-hydrazone equilibrium [9–12], in all of the previously studied Schiff bases these effects were very difficult to detect [35,37]. This is against previous expectations based on the consideration of substituent effects on both the acidity of the proton donating aromatic hydroxyl, and of the basicity of the accepting imine nitrogen [34,37].

Some substituted salicylideneanilines have been previously studied as regards proton transfer in the ground and excited state [20–37]. In this report, we investigate the tautomeric composition in a systematic series of singly and doubly substituted anils of 2-hydroxybenzaldehydes (at C5 and/or C4′, the substituents ranging from strong electron donating to strong electron withdrawing) using a combination of spectroscopic techniques (electronic absorption, fluorescence emission and carbon-13 NMR) and semi-empirical calculations (AM1 for the ground states and INDO/S for the excited states). The results are explained on the basis of a careful consideration of the substituent effects on both pairs of donating/accepting moieties: enol-imine and keto-enamine.

2. Experimental

Compounds **1**–**3**, **7**–**12** and **16**–**18** (Scheme 1 and Scheme 2) were synthesized by condensation of the appropriately 5-substituted 2-hydroxybenzaldehyde with the *p*-substituted aniline in refluxing methanol, followed by recrystallization from benzene. The structures were firmly established on the basis of their ^1H and ^{13}C NMR characteristics in $CDCl_3$.

Electronic absorption spectra were recorded on a Beckman DU 640 spectrophotometer and fluorescence spectra on a Shimadzu RF-5301 PC spectrofluorophotometer, in both cases using 1.00 cm quartz cuvettes. The concentration of the studied



	R_1	R_2
10	NO_2	NO_2
11	H	NO_2
12	MeO	NO_2
13	NO_2	H
14	H	H
15	MeO	H
16	NO_2	MeO
17	H	MeO
18	MeO	MeO

Scheme 2. Structures of model compounds.

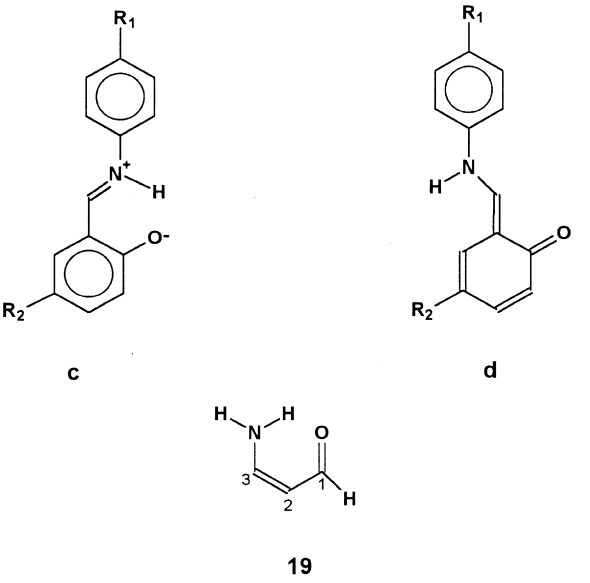
solutions (chloroform) ranged from 1×10^{-5} to 1×10^{-4} mol dm^{-3}. The solvent was carefully purified according to standard procedures.

Solution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 NMR spectrometer operating at nominal frequencies of 200.1 and 50.3 MHz, respectively. All chemical shifts were referenced against TMS.

Ground state geometry optimization and calculation of heats of formation and effective atom charges were done by using the AMPAC package, version 2.10 on a Pentium 150 microcomputer. In all cases the PRECISE option was used. Vertical excitation energies and oscillator strengths were calculated with the aid of INDO/S on the same computer, including configuration interaction (CI) with the first 129 mono-excited singlet states.

3. Results and discussion

It has been previously suggested that the position of the equilibrium **a** = **b** in anils of aromatic α-hydroxyaldehydes is controlled by the acid–base characteristics of both the enol and imine moieties [34,37]. In this regard, the expectations were based on the known fact that electron withdrawing *para*-substituents increase the acidity of a hydroxyl group, and decrease the basicity of an amine group in benzene derivatives. This leads to the prediction that electron withdrawing substituents at C4′ would shift the equilibrium towards **a** and at C5 towards **b** [34]. However, these simple considerations are based on isolated acid–base equilibria, which are absent in the presently studied compounds. When intramolecular acid–base interactions take place between a phenol and an appropriate proton acceptor within the same molecule, but separated from the former by saturated groups, such considerations are highly useful and predictive. This has been shown to be the case in the study of the proton transfer from a phenol to *N*-oxide or to enamine groups, which have been extensively studied by Zundel and coworkers [39,40]. However, it should be borne in mind that in the present case, the accepting –C=N– group is connected to the phenol group in such a way that after the prototropic rearrangement the resultant phenolate no longer maintains its identity. Rather, it rearranges to a keto-enamine form **b**



Scheme 3. Structures of zwitterionic form c, trans-keto form d and model compound 19.

(Scheme 1), where R_2 is now able to interact with a mild electron donating –NH– group. Conversely, R_1 interacts with –C=N– in **a**, and with –NH– (and not with a protonated amino group) in **b** after the tautomeric change occurs. It should be noticed that tautomer **b** has also been proposed to show the zwitterionic and *trans*-keto structures **c** and **d**, respectively [22,23] (see Scheme 3 and the discussion in Section 3.2). This means that the analysis is in this case less simple than previously anticipated. Therefore, we have set out a series of singly and doubly substituted anils at C4′ and/or at C5, in order to address the effects of the substituents R_1 and R_2.

3.1. Electronic absorption and fluorescence measurements

As previously discussed, a shift of the absorption maxima to longer wavelengths is observed in going from **a** to **b** [37]. Since the equilibrium is slow on the electronic absorption time scale, separate bands for each tautomer are observed, at ca. 350 nm for **a** and at 450 nm for **b** [37]. In anils of salicylaldehyde, the equilibrium is significantly shifted towards the imine-enol form **a** [37]. This result is also observed for the presently studied compounds (Table 1), which

Table 1
Solution electronic absorption and fluorescence emission data for compounds **1**–**9**[a]

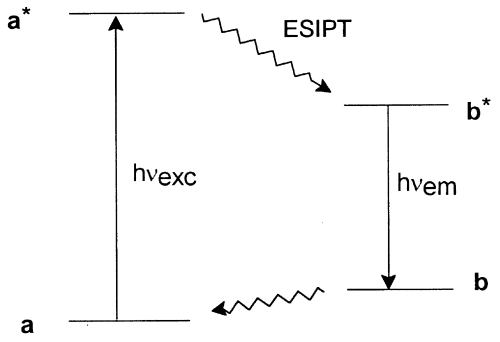
Compound (Form)	Absorption		Fluorescence λ_{em}/nm	Stokes shift $\times 10^{-3}$ cm^{-1}
	λ_{MAX}/nm	$\varepsilon(M^{-1}\ cm^{-1})$		
1(**a**)	345	21620	535	10.3
1(**b**)	460	80	535	3.0
2(**a**)	332	13900	507	10.4
2(**b**)	437	500	507	3.2
3(**a**)	350	16700	507	8.8
3(**b**)	441	670	507	3.0
4(**a**)	357	26250	560	10.2
4(**b**)	486	250	560	2.7
5(**a**)	340	14300	532	10.6
5(**b**)	437	40	525	3.8
6(**a**)	350	21900	522	9.4
6(**b**)	448	50	522	3.2
7(**a**)	388	6140	570	8.2
7(**b**)	483	30	570	3.2
8(**a**)	368	2260	558	9.3
8(**b**)	483	30	558	2.8
9(**a**)	369	6948	557	9.1
9(**b**)	492	30	557	2.4

[a]Solvent: $CHCl_3$.

collects the values of the apparent molar absorptivities for each band for the entire series **1**–**9**. As seen in Table 1, the values of ε at the λ_{MAX} for form **b** are significantly smaller than those corresponding to the λ_{MAX} for form **a**, so that it can be confidently assumed that **a** is the dominating form in all cases. However, the measured values cannot be used to draw quantitative conclusions on the relative amount of form **b** in each case. We therefore believe that previous conclusions [34] based on electronic absorption data for anils **4**–**6** and other *p*-substituted anils of salicylaldehyde should be revised.

The equilibrium **a** = **b** is known to depend on the solvent polarity [20–23,37]. In order to compare with the NMR data, we chose to measure the absorption spectra in $CHCl_3$; the band corresponding to tautomer **b** is less intense in this case (for compound **5** in ethanol, (at 430 nm is 120 M^{-1} cm^{-1} [37], compare with Table 1), but is still observable as a shoulder on the main band for tautomer **a**.

Fluorescence measurements indicate that there is a single emitting species in all cases, since emission is collected at 500–570 nm, irrespective of which band is irradiated (Table 1, minor differences in λ_{em} in **5** are probably unimportant, since all emission bands are broad and show a FWHH of ca. 80 nm). Furthermore, the observed Stokes shifts upon irradiation of the **a** form (Table 1) are indicative that an excited state rearrangement is taking place, since the values are large as compared with normal Stokes shifts of vibrational origin which correspond to irradiating **b** forms. The rearrangement is strongly implied to be the proton transfer conversion **a*** → **b***, as in previous cases. This excited state intramolecular proton transfer process (ESIPT) can be pictured by adapting a general Förster cycle, as in Scheme 4 [41,42]. The existence



Scheme 4. Forster cycle adapted to proton transfer.

of such a cycle is also in agreement with semi-empirical calculations of the properties of both the ground and excited states of the studied molecules (see below).

3.2. Semi-empirical MO calculations

Ground state properties for compounds **1**–**9** were studied with the aid of the AM1 program, capable of taking into account strong hydrogen bonding interactions [43]. The corresponding heats of formation of both tautomeric forms and heats of tautomerization are shown in Table 2. In all cases, the enol imine form **a** is predicted to be dominant, in qualitative agreement with electronic absorption spectroscopy.

Table 2
Heats of formation of tautomeric forms and heats of tautomerization for compounds **1**–**9**, and net atomic charges in compounds **5a**,**b** and **19** according to semi-empirical calculations using the AM1 method[a]

Compound	ΔH_b^0 kJ.mol^{-1}	ΔH_a^0 kJ.mol^{-1}	$\Delta\Delta H^0$ kJ.mol^{-1}
1	167.6	155.1	12.5
2	143.1	134.6	8.5
3	−14.7	−25.1	10.4
4	155.3	138.2	17.1
5	139.2	122.5	16.7
6	−17.3	−36.6	19.3
7	−1.7	−14.6	12.9
8	−16.6	−30.7	14.1
9	−173.1	−189.7	16.6
	Net atomic charges in compounds **5** and **19**		
Atom	Form **5a**	Form **5b**	**19**[b]
C1	−0.165	−0.292	−0.430(C2)
C2	+0.149	+0.306	+0.235(C1)
C3	−0.177	−0.230	
C4	−0.076	−0.060	
C5	−0.180	−0.191	
C6	−0.071	−0.059	
C1′	−0.004	+0.061	
C2′,6′	−0.098	−0.163	
C3′,5′	−0.130	−0.098	
C4′	−0.125	−0.150	
C7	+0.016	+0.121	+0.106(C3)
O	−0.257	−0.387	−0.366
N	−0.206	−0.233	−0.373

[a] $\Delta H_{a,b}^0$ are the heats of formation of forms **a** and **b**, and $\Delta\Delta H^0 = \Delta H_b^0 - \Delta H_a^0$ is the heat of tautomerization.
[b] Carbon numbering according to Scheme 3 in parenthesis.

On comparing the heats of tautomerization in the studied series, the following conclusions can be drawn. Almost no shift in the tautomeric equilibrium is predicted on changing the electronic demand of R_1 (Table 2, compare compounds **4**, **5** and **6**). The presence of other substituents at C4′ led to similar conclusions [35]. This may seem surprising in view of the strong effects of *p*-substituents on the basicity of aromatic amino groups. However, consideration of the net atomic charges calculated by AM1 may shed some light on the subject. AM1 geometry optimization of aniline and anilinium ion gives net atomic charges at the *para* carbon of −0.193 and −0.063, respectively, i.e., a difference of 0.130 units, itself constituting the basis for the effect of *p*-substituents on the basicity of anilines. However, the net atomic charges at C4′ in both forms of the parent anil **5** yield a much smaller difference of 0.025 units in going from **a** to **b** (Table 2). This may be the origin of the relative insensitivity of the equilibrium **a** = **b** with respect to R_1.

Concerning the effect of R_2, AM1 geometry optimization of phenol and phenolate anion gives net atomic charges at the *p*-carbon of −0.166 and −0.339, respectively, i.e., a difference of 0.173 units. This large difference, responsible for the increased acidity of *p*-nitro phenol as compared with phenol, is not observed in compound **5**. According to Table 2 the effect at C5 is much smaller (0.011 units). However, the negative charges at the critical carbons C1 and C3 in form **b** are significantly larger than in form **a**, and therefore an electron withdrawing group at C5 would be able to preferentially stabilize form **b**. Indeed, on comparing the values of $\Delta\Delta H^0$ for compounds **2**, **5** and **8**, a shift to form **b** is predicted for the 5-NO_2 substituted anil **2**, though $\Delta\Delta H^0$ is still positive. A similar shift is also predicted for compounds **1** and **3**, where $R_2 = NO_2$. It may be noticed that this result is only accidentally coincident with the predictions based on the acidity of phenols (see above), since the effects of R_2 on the quinoid ring of form **b** are difficult to predict *a priori*. Tautomer **b** has also been proposed to display a zwitterionic structure **c** (Scheme 3), where the oxygen-containing ring is in fact a phenolate anion. However, the optimized bond distances around the critical moiety O-C2-C1-C7-N in **5b** also correspond to a formal keto-enamine (C–O, 1.251 Å, C2–C1, 1.464 Å; C1–C7, 1.385; Å

Table 3
Semi-empirical calculations using the INDO/S method for compounds **1**–**9**

Compound (form)	λ_{MAX}/nm	f [a]
1(**a**)	307	1.00
1(**b**)	378	0.78
2(**a**)	302	0.84
2(**b**)	381	0.67
3(**a**)	307	1.00
3(**b**)	386	0.72
4(**a**)	314	1.00
4(**b**)	368	0.74
5(**a**)	303	0.94
5(**b**)	367	0.58
6(**a**)	304	1.00
6(**b**)	372	0.62
7(**a**)	322	0.96
7(**b**)	383	0.72
8(**a**)	308	0.64
8(**b**)	399	0.56
9(**a**)	314	0.84
9(**b**)	385	0.61

[a]Oscillator strength.

and C7–N, 1.355 Å) [35] (compare with model **19**, Scheme 3: C–O, 1.243 Å, C1–C2, 1.443 Å; C2–C3, 1.367; Å and C3–N, 1.353 Å). Further, as seen in Table 2, the distribution of charges in **5b** is typical of the keto-enamine structure **19**. The keto form has also been proposed to adopt the *trans* configuration **d** (Scheme 3), particularly in solid photochromic materials [32,37]. However, AM1 optimization yields heats of formations for all *trans* keto isomers **1d–9d** which are ca. 15 kJ.mol^{-1} higher than those corresponding to the *cis* forms **b**, presumably due to the loss of the internal hydrogen bond in going from **b** to **d**.

As regards the excited states, INDO/S calculations including configuration interaction were carried out on the fully optimized geometries of all compounds, with the results shown in Table 3. The INDO/S method represents an improved version of the CNDO/S method, and has been successfully applied to related systems [44,45]. In all cases, the allowed p–p* transition of lower energy occurs at longer wavelengths in form **b** than in form **a**, in good agreement with the experiments.

3.3. C NMR spectroscopy

^{13}C NMR Spectroscopy has been previously applied to monitor the position of the tautomeric equilibrium in series of compounds which are structurally related to compounds **1**–**9**, such as arylazo phenols and naphthols [9–12] and anils of 2-hydroxynaphthalene-1-carbaldehyde and 10-hydroxyphenanthrene-9-carbaldehyde [32–35]. The success in applying ^{13}C NMR stems from the high sensitivity of certain carbon chemical shifts to the position of the

Table 4
Solution ^{13}C NMR chemical shifts for compounds **1**–**9**

Carbon	Chemical shift[a]								
	Compound								
	1[b]	**2**[b]	**3**[b]	**4**[c]	**5**[c]	**6**[c]	**7**[b]	**8**[b]	**9**[b]
1	117.7	117.9	116.1	118.6	119.0	119.2	116.1	116.7	118.6
2	167.1	166.7	166.7	161.2	160.9	160.8	152.4	152.1	152.0
3	116.5	116.1	116.1	117.4	117.0	116.9	116.3	117.7	117.7
4	128.8	128.2	127.8	134.3	132.9	132.5	122.0	120.3	119.8
5	140.3	139.8	139.1	119.4	118.8	118.8	155.5	155.3	155.0
6	129.3	128.2	127.8	132.9	132.1	131.8	115.3	115.3	115.0
7	163.6	160.4	157.8	165.2	162.4	160.2	165.0	162.2	159.8
1′	152.6	146.5	139.7	154.0	148.2	141.1	154.1	148.4	141.2
2′,6′	121.9	121.0	122.4	121.7	121.0	122.1	121.7	121.0	122.1
3′,5′	125.3	129.5	114.7	125.0	129.2	114.4	125.1	129.2	114.4
4′	142.6	127.9	159.61	145.9	126.7	158.6	146.0	126.7	158.7

[a]Values in ppm vs. TMS; solvent: $CDCl_3$.
[b]This work.
[c]Ref. [35].

Table 5
^{13}C NMR Chemical shifts for C2 in compounds **10**–**18**, and corrected values for compounds **1**–**9**

Chemical shift/ppm								
Compound								
10[a]	**11**[a]	**12**[a]	**13**[b]	**14**[b]	**15**[b]	**16**[a]	**17**[a]	**18**[a]
134.4	133.8	133.9	130.4	130.2	129.8	121.5	121.7	121.5
Corrected chemical shift/ppm[c]								
Compound								
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
162.9	163.1	163.0	161.0	160.9	161.2	161.1	160.6	160.7

[a]This work.
[b]Ref. [47].
[c]Values were corrected using the equation $\delta(\text{corr}) = \delta - [\delta\text{d}(\text{model}) - \delta(\mathbf{14})]$, where δ is the observed value in a given compound in the series **1**–**9**, δ(model) is the value in the analogously subsituted model **10**–**18**, and δ(**14**) is the value in the parent compound **14**.

equilibrium **a** = **b**, and from the knowledge of the intrinsic values for the tautomeric forms. Specifically, carbon C2 should show a value of ca. 160 ppm in an unsubstituted **a** form, whereas the corresponding value in the **b** form is ca. 180 ppm [34]. In the presently studied systems, we need to apply corrections in order to separate intrinsic substituent chemical shift (SCS) effects from substituent induced equilibrium shifts. Since the phenol ring of form **a** is highly substituted, SCS effects for monosubstituted benzene as found in usual correlation tables [46] may not be adequate to correct for C2. We therefore used a different strategy, based on a consideration of the model compounds **10**–**18** (Scheme 2), in which tautomerism is absent. We corrected the chemical shift for C2 using the following expression:

$$\delta(\text{corr}) = \delta - [\delta(\text{model}) - \delta(\mathbf{14})]$$

where δ is the observed value in a given compound within the series **1**–**9**, δ(model) is the value in the analogously subsituted model **10**–**18**, and δ(**14**) is the value in the parent unsubstituted compound **14**. Once corrected for these effects, the chemical shift is compared with the extreme value of 160 ppm for **a** in order to search for a possible equilibrium shift towards **b**. The observed carbon chemical shifts in **1**–**9** are reported in Table 4, and the corresponding values in **10**–**18** for C2, as well as the corrected C2 chemical shifts for **1**–**9** are collected in Table 5.

According to the results presented in Table 5, there is a slight but significant displacement of the equilibrium towards the **b** form in compounds **1**–**3**. Interestingly, these are the compounds where a shift to form **b** has been predicted above on the basis of AM1 calculations.

4. Conclusions

A series of singly and doubly substituted anils of 2-hydroxybenzaldehyde have been studied by electronic absorption, fluorescence emission and ^{13}C NMR spectroscopies, and by semi-empirical MO calculation of the ground (AM1) and excited (INDO/S) state properties. The existence of a proton transfer (ESIPT) reaction in the excited state has been established, and the theoretical predictions have been found to be in good agreement with the experiments. Substituent effects on the ground state tautomeric equilibrium have also been investigated, and minor shifts towards the keto-enamine form have been found on the basis of ^{13}C NMR spectroscopy, in agreement with AM1 predictions [46].

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