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Intramolecular Proton or Hydrogen-Atom Transfer in the Ground and Excited States of 2-Hydroxybenzoyl Compounds[†]

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Potential energy surfaces for the intramolecular proton transfer of ground (GSIPT) and excited (ESIPT) states of 2-hydroxybenzoyl compounds were obtained. Based on the results, intramolecular proton transfer in this type of compound is strongly dependent on the distances between the oxygen atoms that bear the intramolecular hydrogen bond (IMHB). Also, the GSIPT curves for these compounds contain a single minimum that is located in the zone for the normal (enol) form. The ESIPT curves also contain a single minimum but lie in the zone for the keto form. There is no correlation between the strength of the IMHB and the proton transfer barrier through it. The energy for the excited singlet $1(n,\pi^*)$ for these compounds is strongly dependent on the resonance effect of the substituent, −R, so this state is the first excited singlet only in derivatives with nearly nonresonating R. The ESIPT processes are of the proton transfer type, even though the final form possesses no zwitterionic connotations. Finally, these theoretical features are quite consistent with photophysical experimental evidence for this type of compounds.

1. Introduction

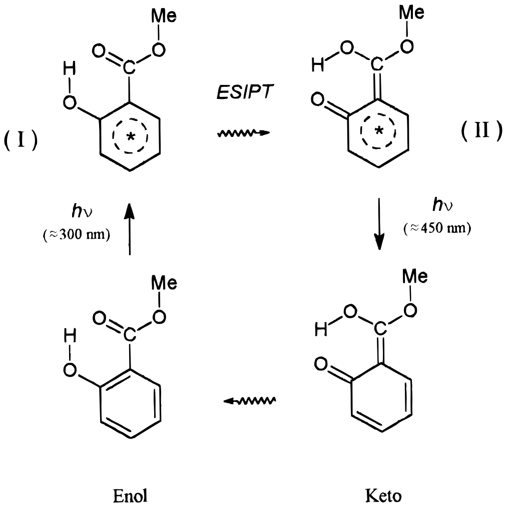
More than 40 years ago, Albert Weller,[1] using a 2-hydroxybenzoyl compound [Ph(OH)COR] such as methyl salicylate, laid the foundation for the subsequently called "excited-state intramolecular proton transfer" (ESIPT) mechanism (Scheme 1). This mechanism is currently being employed to understand the behavior of some compounds that exhibit such interesting properties as ultraviolet stabilization,[2−7] stimulated radiation production,[8,9] and information storage,[10] as well as environmental probes in biomolecules.[11]

The signature of an ESIPT process is the emission of strongly Stokes-shifted fluorescence following absorption of UV photons. This spectral feature is the result of both the exothermal behavior of the excited singlet state potential curve that governs the ESIPT process while the proton transfer develops, and the endothermal behavior of the potential curve for the process in the ground state (GSIPT). These combined effects bring the two electronic states involved in the emission dramatically nearer. While the curve for the excited electronic state is that which dictates whether the proton phototransfer is to take place, the role played by the curve for the ground electronic state is spectroscopically as relevant because it contributes to the Stokes shift and is responsible for the spectral envelope with no vibronic structure that is observed in the fluorescence of compounds undergoing an ESIPT process.

2-Hydroxybenzoyl compounds possess a strong intramolecular hydrogen bond (IMHB) as a result of their bearing a hydroxyl group and a carbonyl group that act as a proton donor (acid) and acceptor (base), respectively, in adjacent positions. It is widely accepted that the presence of this strong IMHB endows the structure with increased photostability, which in turn is partly responsible for the interesting, characteristic properties of these compounds.

According to Weller,[1,12] the acid−base properties of the hydroxyl and carbonyl groups on an aromatic ring can change to such an extent by the effect of electronic excitation that the hydrogen atom in the hydroxyl group (structure I in Scheme 1) may shift to the vicinity of the oxygen atom in the carbonyl group (structure II in Scheme 1), thereby giving rise to a proton phototransfer and the consequent formation of a zwitterionic structure. The proton transfer takes place via the IMHB; the ease with which it does increases with increasing bond strength, which in turn is dictated at first by the acidity and basicity of the two groups involved in the IMHB.

SCHEME 1



The energy curves that describe the displacement of the hydrogen atom in the ground (GSIPT) and excited states (ESIPT) play central roles in the photophysics of 2-hydroxybenzoyl compounds and as such have aroused much attention in both the experimental and theoretical domains.

There is currently accepted evidence[13,14] that the GSIPT curves for 2-hydroxybenzaldehyde (−H), 2-hydroxyacetophenone (−Me), methyl salicylate (−OMe), and salicylamide ($-NH_2$) (see Scheme 2) exhibit a single minimum that is located in the zone for the enol form—the normal form (I in Scheme 1)—whereas their ESIPT curves, which control the fluorescent

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[†] This paper is dedicated to the memory of Albert Weller, who passed away in September 1996, in appreciation of his pioneering research into such an interesting topic as proton phototransfer (ESIPT) processes.

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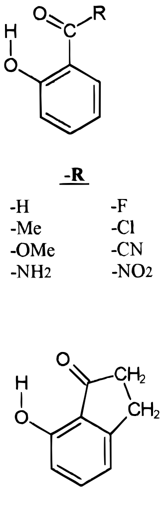
SCHEME 2



state, and also contain a single minimum, however, lie in the zone for the keto form, which is also the transferred form (II in Scheme 1). Also, there is evidence based on the heavy atom effect, quantum yields, and lifetimes,[15] as well as on the rate constants for the proton transfer process,[16] that the first singlet electronic state for 2-hydroxybenzaldehyde (−H) and 2-hydroxyacetophenone (−Me) is of the n,π^* type whereas that for the other compounds is of the π,π^* type. The nature of the state that governs the phototransfer is quite important since an n,π^* state is believed to facilitate hydrogen abstraction whereas a π,π^* state is thought to facilitate the proton transfer.[17]

One exception among 2-hydroxybenzoyl compounds is 7-hydroxy-1-indanone (7HIN), which can be assimilated to 2-hydroxyacetophenone with a lengthened IMHB through the presence of an ethylene bridge between the carbon atom in the carbonyl group and carbon 6 in the aromatic ring (see Scheme 2). Experimental evidence gathered for this compound makes it highly interesting. In fact, Itoh et al.,[18] using two-step laser excitation (TLSE) and transient absorption techniques, concluded that the ground electronic state for the 7HIN keto form in methylcyclohexane and tetrahydrofuran is a metastable state, so its GSIPT curve contains a double minimum. However, Chow et al.[19] contradicted this interpretation in assigning the transient species to a triplet state of the transferred form of the compound. On the other hand, Nishima et al.[13] could not ascertain whether the ESIPT curve for this compound in a durene matrix at 4.2 K contained two minima. It should be noted that a computation at the HF level using a 3-21G base provided a double-minimum GSIPT curve.[20]

It is currently accepted[21−23] that realistic estimation of the GSIPT and ESIPT curves for this type of compound entails the use of electron correlation—at least at the level of the second-order perturbation theory (MPS, CASPT2, CIS-MP2)—in the calculations because computations for these molecular structures at the HF, CASSCF, and CIS levels lead to GSIPT and ESIPT curves with two minima located in the zones for the enol and keto form, respectively. Recently, our group [23] demonstrated that the GSIPT curve for 2-hydroxyacetophenone can be accurately established from B3LYP calculations.

In this work, we undertook a theoretical study of a number of 2-hydroxybenzoyl compounds [viz. Ph(OH)CO-R, with −R = −H, −Me, −OMe, $-NH_2$, −Cl, −F, −CN, and $-NO_2$] (see Scheme 2), in order to obtain evidence for determining (*a*) whether the GSIPT and ESIPT curves that describe the fluorescent behavior of these compounds contain one or two minima; (b) whether the shape of the curves and the strength of the IMHB depend on the electronic nature of the substituent; (c) whether the process involved is a proton transfer or a hydrogen atom transfer; and (d) the effect on the GSIPT and ESIPT curves of a lengthened distance for the hydrogen bond caused by the presence of an ethylene bridge in 7HIN.

2. Computational Section

Hybrid HF/DFT methods have been proposed as reliable tools for electronic computation in a general protocol for studying static and dynamic properties of hydrogen-bonded systems.[24] One such method, B3LYP,[25,26] was recently evaluated in intramolecular hydrogen bonding studies[27] and found to result in good agreement between DFT and MP2 results for structural and energy parameters. As regards the thermochemistry of intramolecular tautomerism, in the enol−keto equilibrium between 2-hydroxypyridine and 2-pyridone, which calls for higher post-HF methods than MP2 in order to ensure consistency with experimental facts, the B3LYP model was found to provide results close to those of the most sophisticated post-HF models.[28]

The B3LYP method (Becke's three-parameter functional[25] using the Lee−Yang−Parr correlation functional[26]) in combination with the 6-31G** basis set has been used to obtain optimized geometries and vibrational frequencies for stable structures. Evaluating potential energy surfaces that describe the proton movements entails molecular structure optimization; in fact, the ground state intramolecular proton transfer (GSIPT) curves constructed at a fixed O−O distance have been found to be inappropriate descriptors for this type of system.[23] We constructed ground-state proton transfer curves (GSIPT) for the energies of the B3LYP/6-31G** optimized structures of the compounds at fixed O_{phenol}−H distances over the 0.85−1.6 Å range.

The strength of the intramolecular hydrogen bond (IMHB) in the stable form of each molecule studied was evaluated as (*a*) the difference between the B3LYP/6-31G** energy for the stable structure with the phenol group rotated by 180° and the rest of the molecule frozen and the energy for this stable form optimized at the B3LYP/6-31G** level; and (b) the difference between the energies for the previous open and closed forms, both fully optimized at the B3LYP/6-31G** level.

Information on the ESIPT mechanism was obtained by calculating the Franck−Condon transition energies for the B3LYP/6-31G** ground-state structures at the CIS/6-31G** level.[29] The Franck−Condon curves for the proton transfer were obtained by adding the CIS/6-31G** excitation energies to the GSIPT curves.

All computations were done with the aid of the Gaussian 94 software package.[30]

3. Results and Discussions

3.1. GSIPT and ESIPT Curves vs Photophysics. Recent evidence on the molecular structure of 2-hydroxy-5-methylphenyl-2′-benzotriazole (Tinuvin P),[31] 2-hydroxyacetophenone,[23] and 2-hydroxyacetonaphthone [32] suggests the need to include the effect of electronic correlation at the MP2 or B3LYP level on the 6-31G** base in order to obtain a correct description of the experimental structure of these compounds, which exhibit strong IMHBs. In addition, these calculations provide an appropriate description of the IR spectra for these compounds.[33] These latter are consistent with recent findings of Lampert et al.,[34,35] who found the vibrational frequencies for various 2-hydroxybenzoyl compounds to be accurately described in theoretical terms at the B3LYP/6-31G** level. No further comment on this type of date will thus made be in this paper.

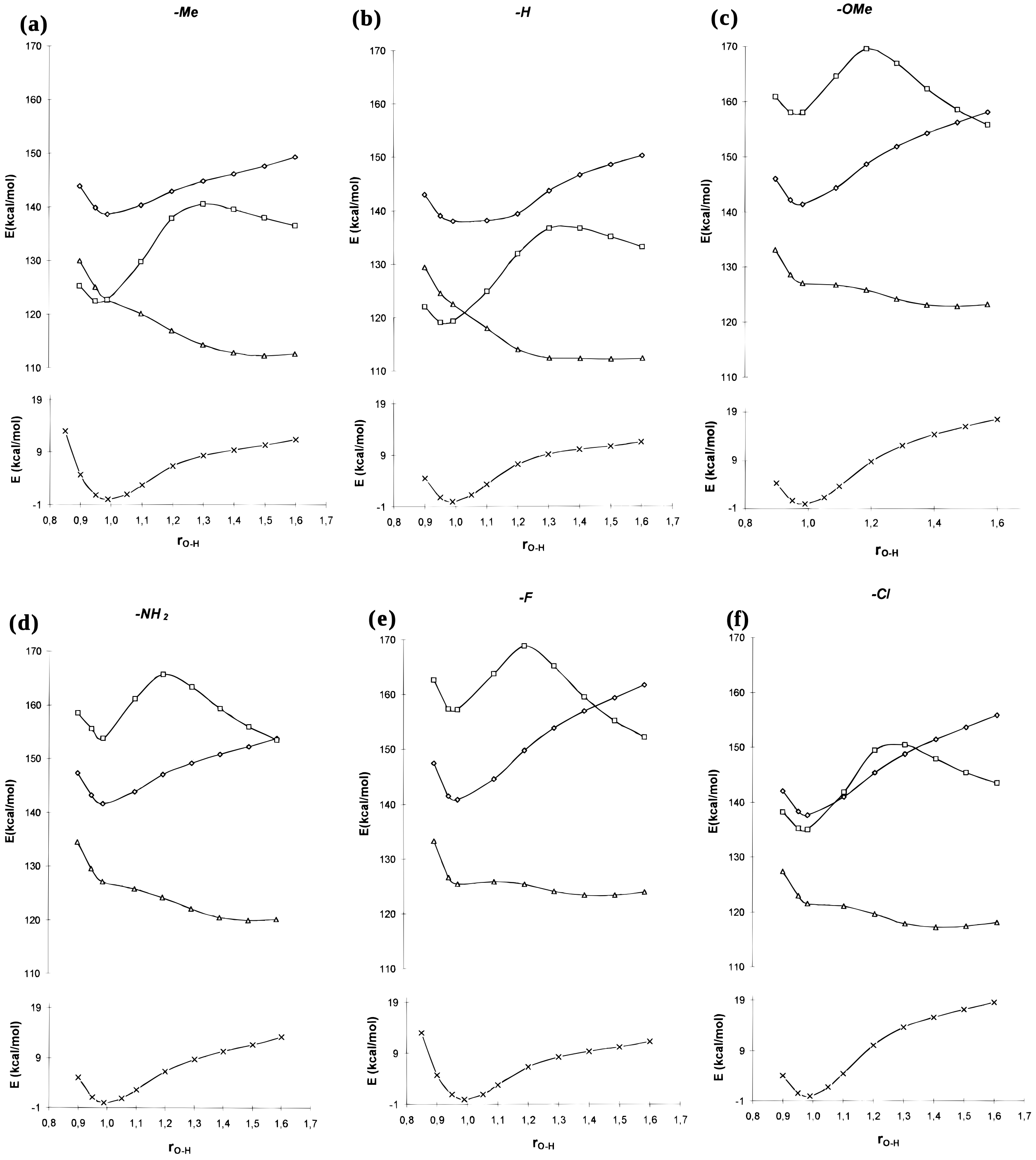
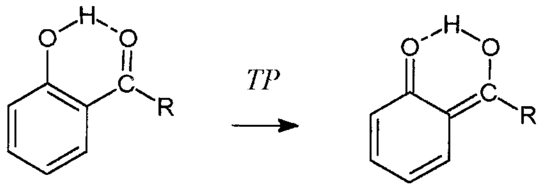


Figure 1. GSIPT curves (-×-) obtained from B3LYP/6-31G** optimized structures and $(n,\pi^*)^1$ (-□-), $1(\pi,\pi^*)^1$ (-△-), and $2(\pi,\pi^*)^1$ (-◇-) Franck–Condon ESIPT curves constructed by adding CIS/6-31G** transition energies to B3LYP/6-31G** energies for the GSIPT curves of the 2-hydroxybenzoyl compounds. r_{O-H} in Å.

Figure 1 shows the results obtained for the GSIPT curves of the compounds studied. Their analysis reveals that all contain a single minimum that is invariably located in the zone corresponding to the enol form of the compound. Note that the substituents involved (R) ranged from a strong electron donor such as the amino group to a fairly strong acceptor such as the cyano group. This is especially relevant since experimental evidence suggests that such is indeed the situation for −H, −Me, −OMe, and $-NH_2$.[13,14]

One very interesting inference of the analysis of the change undergone by the molecular structure of these compounds as the transfer progresses is that such a structure, whatever the electronic nature of substituent R, changes gradually from the enol form to a typically keto form at an r_{O-H} distance of 1.6 Å, even though no energy minimum is present in this zone. It is especially interesting that, while the length of the IMHB (i.e. the distance between the oxygen atoms that bear it) is virtually the same for the enol and keto forms, the proton transfer results in considerable shortening of the O−O bond length, which peaks halfway through the transfer (viz. at $r_{O-H} = 1.3$ Å, see Figure 2). The closer approach of the oxygen atoms at the transfer midpoint is favored energetically. Failure to permit this approach might lead one to expect a barrier where none is present. This result advises against obtaining proton transfer curves at a fixed distance between the heteroatoms that bear the IMHB, as previously shown elsewhere.[23]

Worth special note is also the fact that the relative instability of the transferred zone relative to the energy minimum in the



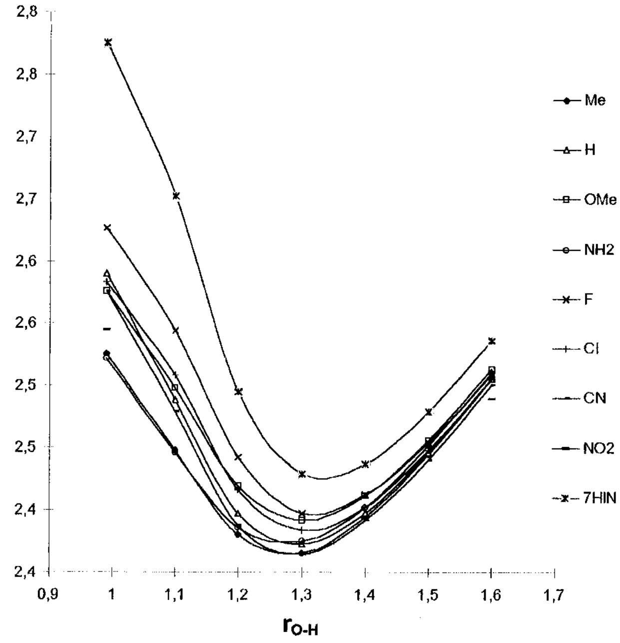


Figure 2. Variation of the IMHB lengh (O−O bond) in the ground-state proton transfer for 2-hydroxybenzoyl compounds calculated at the B3LYP/6-31G** level. Bond distances in Å.

GSIPT curve varies with the substituent R. We shall analyze this fact later on, simultaneously with the examination of the effect of the electronic nature of the substituent on the IMHB strength.

If the geometry of the hydrogen bond is correctly described by the B3LYP/6-31G** results[23,31−35] and the structural change that takes place along the GSIPT curve appears to accurately describe the expected change for the transfer in the excited electronic state, then it seems appropriate to estimate the ESIPT curve as a Franck−Condon curve for the GSIPT curve by using the CIS method to evaluate the transitions involved. Figure 1 shows the ESIPT curves thus obtained for the first three singlet states. Invariably, all the compounds studied exhibited one n,π^* state and two π,π^* states. First of all, we must emphasize that the first state, $(\pi,\pi^*)^1$, was that which clearly described the transfer toward the keto form. For all the compounds studied, this ESIPT curve contained a single minimum (located in the zone for the keto form); the minimum was highly exothermal (about 20 kcal/mol) relative to the enol form, which was that produced in the absorption process. Also, these $1(\pi,\pi^*)^1$ curves posed no barrier to the proton transfer. This last finding is especially relevant because it contradicts the previous hypothesis[21,22] that correlation effects of at least second order must be used in order to eliminate proton transfer barriers in the first π,π^* excited electronic state—these computations are very expensive or even unfeasible in many cases. We must emphasize the significance of these results since an ESIPT curve with a single minimum located in the transferred zone coincides with the experimental facts for −H, −Me, −OMe, and $-NH_2$.[13,14]

The energy differences for the electronic transitions for the enol and keto forms (an r_{O-H} distance of 1.6 Å was adopted for the latter) provided by the CIS method allowed the theoretical estimation of the Stokes shifts for these compounds. Although the estimated shifts were somewhat large (see Table 1), they were smaller than their experimental counterparts.[13,36−38]

TABLE 1: Stokes Shifts (10^3 cm^{-1}) for 2-Hydroxybenzoyl Compounds As Calculated from the CIS/6-31G Excitation Energies of B3LYP/6-31G** Enol and Keto (r_{OH} = 1.6 Å) Optimized Structures of the Ground State and Experimental Values Obtained in (1) Cyclohexane at Room Temperature, and (2) Durene Mixed Crystals at 4.2 K**

		experimental value	
molecule	theor values	at room temp	at 4.2 K
−Me	7.52	11.25[a]	10.30[b]
−H	7.34	11.53[a]	
−OMe	7.51	10.44[a]	9.60[b]
$-NH_2$	7.05	10.54[a]	9.60[b]
−Cl	7.71	10.88[c]	
−F	7.26		
−CN	7.76		
$-NO_2$	8.36		
7HIN	8.46		12.40[b]

[a] From ref 36. [b] From ref 13. [c] From ref 38.

It should be noted that the curves of Figure 1 are quite consistent with experimental facts; thus, while the first excited singlet state in −OMe and $-NH_2$ is of the π,π^* type,[15,16] that in −H and −Me is of the n,π^* type.[15,16] Based on the ESIPT curves obtained, the comparatively low fluorescence quantum yield for salicyloyl chloride (−Cl)[38] can be ascribed to a heavy atom effect[39−42] since the first excited electronic state for the compound was of the π,π^* type.

3.2. GSIPT Curves *vs* IMHB Strength. In principle, one plausible working hypothesis is assuming that the stronger the IMHB in 2-hydroxybenzoyl compounds is, the easier will be the proton transfer since the stronger the bond is, the shorter it should be as the likely result of the increased acidity of the phenol group or basicity of the carbonyl group. Based on this hypothesis, it seems logical to rationalize the behavior of the GSIPT and ESIPT curves for these compounds in energy terms on the basis of the strength of their IMHB.

Let us first evaluate the strength of the IMHB in these compounds. To this end, we shall adopt two different molecular structure references:

(a) The compound in the absence of an IMHB, i.e., with the phenol group rotated by 180° (open form) relative to its enol (closed) form but with the rest of the molecular geometry in a frozen state. We shall use $\Delta E_{IMHB(NO)}$ to denote the B3LYP/6-31G** energy difference between the two structures.

(b) The fully optimized open form. The energy difference assigned to the IMHB, $\Delta E_{IMHB(O)}$, will thus be the difference between the values corresponding to two B3LYP/6-31G** energy minima.

Figure 3 shows a plot of $\Delta E_{IMHB(NO)}$ against $\Delta E_{IMHB(O)}$ for the compounds studied (the individual values are given in Table 3). If the data for $-NH_2$ is excluded, then consistency is excellent ($n = 7$, $r = 0.998$, sd = 0.12 kcal/mol). The deviation of $-NH_2$ in Figure 3 is a result of the open form of this compound being significantly stabilized by shifting the amido group off the molecular plane, which markedly decreases $\Delta E_{IMHB(O)}$; however, from the fitting obtained we can estimate the value for this term should this unexpected alteration not ascribable to the IMHB strength not occur (see Table 2).

The substituents −R considerably alter the IMHB strength in the compounds studied (by about 6.5 kcal/mol). There is no correlation between these quantities, $\Delta E_{IMHB(NO)}$ and $\Delta E_{IMHB(O)}$, the shape of the above-described GSIPT curves (or, for that

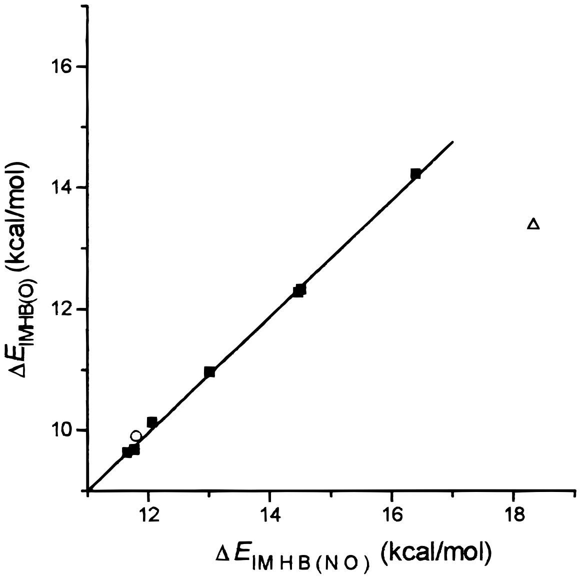


Figure 3. Plot of $\Delta E_{IMHB(NO)}$ vs $\Delta E_{IMHB(O)}$ for the 2-hydroxybenzoyl compounds studied: (■) −H, −Me, −OMe, −F, −Cl, −CN, $-NO_2$, (△) $-NH_2$, (○) 7HIN.

matter, with the ease with which the proton transfer takes place in these molecular system, $\Delta E_{barrier}$,see below).

3.3. Analysis of the Substituent Effect. One appropriate way of systematizing the substituent effect could be to use the model of Taft and Topsom[43] based on the intrinsic resonance, inductive field, and polarizability effects that characterize the behavior of a substituent according to these authors. Recently, this model was successfully applied to widely diverse chemical problems.[44−47] We shall use it here to analyze calculated parameters of relevance to the photophysical behavior of the compounds studied (viz. the IMHB strength and GSIPT curves, as well as changes in the energies for the singlet electronic transitions). Table 2 gives the parameters analyzed below.

A preliminary analysis of the IMHB strength values given in Table 2 allows us to conclude that those for acceptor groups (−CN and $-NO_2$) are markedly deviant from the expectations (the two groups actually behave as if they were electron donors). In fact, the other 10 substituents can be accurately described simply from their resonance and inductive field effects:

$$\Delta E_{IMBH(O)} = -6.94(\pm 1.02)\sigma_R - 10.68(\pm 1.19)\sigma_F + 13.01 \quad (1)$$

with $n = 10$, $r = 0.971$, and sd = 0.56 kcal/mol (including CN and NO_2 leads to $r = 0.866$ and sd = 1.15).

In conclusion, based on eq 1, the substituent increases the IMHB strength by its resonance effect and decreases it by its inductive field effect. The polarizability thus seems to be uninfluential. All this is seemingly normal since resonance effects increase the basicity of the carbonyl oxygen and inductive effects deactivate its lone pair. In principle, the somewhat anomalous behavior of the CN and NO_2 groups can be ascribed to the absence of a resonant effect on the carbonyl group, which allows it to meet its π electron requirements from the aromatic system,[45] thereby strengthening its IMHB at the expense of the phenol system, which possibly increases in acidity. One alternative explanation is the presence of strong dipole−dipole interactions produced by the large dipole moments of these groups, which will increase ΔE_{IMHB}.

Let us now examine the relationship between the IMHB strength and the instability produced by the proton transfer, evaluated as the difference between the energy corresponding to $r_{O-H} = 1.6$ Å and the minimum energy (i.e. that at $r_{O-H} \simeq 0.99$ Å), which we shall denote by $\Delta E_{barrier}$. Surprisingly (see Table 2), the two parameters are not correlated. However, it is interesting to note that the inductive field effect of the substituent is acceptably accurately described by this quantity. Thus,

$$\Delta E_{barrier} = 17.44(\pm 2.27)\sigma_F + 11.52 \quad (2)$$

with $n = 6$ (NH_2, OMe, Me, H, F, and Cl), $r = 0.968$, and sd = 1.02 kcal/mol. Again, the CN and NO_2 groups were excluded from the fit because they exhibited the same anomalous behavior as regards their inductive effect.

Let us analyze the dependence on the substituent of the energy of the electron transitions to the first excited singlet states, which govern the photophysics of these molecular systems. The energy for the theoretical transitions $(n,\pi^*)^1$ and $1(\pi,\pi^*)^1$ from the stable structure (enol form) is surprisingly well described by this model (with all the groups included in the fit except the nitro group, because its n,π^* transition exhibits a strong contribution from it). Thus,

$$\tilde{\nu}[(n,\pi^*)^1] = -26.12(\pm 4.45)\sigma_R + 7.40(\pm 3.86)\sigma_F + 10.17(\pm 4.26)\sigma_\alpha + 42.89 \quad (3)$$

with $n = 7$, $r = 0.972$, and sd = 2.13 × 10^3 cm^{-1}.

Also

$$\tilde{\nu}[1(\pi,\pi^*)^1] = -5.85(\pm 1.67)\sigma_R - 3.40(\pm 1.32)\sigma_F + 1.99(\pm 1.66)\sigma_\alpha + 43.00 \quad (4)$$

with $n = 8$, $r = 0.944$, and sd = 0.84 × 10^3 cm^{-1}.

We should emphasize that, based on eq 3, the n,π^* transition is strongly shifted hypsochromically by effect of the substituent resonance. By contrast, the polarizability effect is the only one that causes a bathochromic shift. This may be the reason only the first singlet is of the n,π^* type in −H, −Me, −CN and $-NO_2$, the sole compounds whose substituents lack a resonance effect. On the other hand, the π,π^* transition (eq 4) is shifted hypsochromically by resonance and bathochromically by inductive and polarizability effects.

3.4. Proton Transfer *vs* Hydrogen Transfer. The results obtained in this work shed some light on this aspect of the ESIPT mechanism. Careful analysis of the computations performed to construct the GSIPT curves reveals that the geometry adapts from a phenolic (enol) structure to a typical keto structure as the transfer develops. Also, if intermediate points in the transfer shorten the distance between the heteroatoms that bear the IMHB, the hydrogen atom is never fully exposed. In fact, the analysis of the electron charge on this atom during the transfer reveals that it changes only slightly in the process. However, from Figure 1 it also follows that the sole state that can describe a transfer toward the transferred zone is the first π,π^* state. The situation would be different if the state controlling the transfer were of the n,π^* type; in such a case it would be reasonable to expect processes of intramolecular hydrogen atom abstraction.[17] However, as can be seen from Figure 1, the curves $(n,\pi^*)^1$ become markedly unstable as the transfer develops and, even though they fall to a minimum in the transferred zone, the underlying ESIPTs can never compete with those described by the first ESIPT curve of the π,π^* type. This conclusion is consistent with the results of Nagoaka et al.[16]

Let us return to Weller's original hypothesis based on acidity and basicity changes in the groups involved in the electronic excitation of the molecular system and use benzaldehyde and phenol as our models. Table 3 gives basicity data calculated for the different electronic states of interest for benzaldehyde

TABLE 2: Calculated Parameters for the 2-Hydroxybenzoyl Compounds Studied, Used in the Analysis of the Substituent Effect: Strength of the IMHB with [$\Delta E_{IMHB(O)}$] and without [$\Delta E_{IMHB(NO)}$] Optimization of the Open Structure (in kcal/mol); Energy Difference between the Enol and Keto Forms, $\Delta E_{barrier}$ (kcal/mol); CIS/6-31G//B3LYP/6-31G** Transition Energies $\tilde{\nu}[1(\pi,\pi^*)^1]$ and $\tilde{\nu}[1(\pi,\pi^*)^1]$ from Stable Molecular Structure, and Parameters for the Resonance Effect (σ_{R^+}), Inductive Field Effect (σ_F) and Polarizability Effect (σ_α) of the Substituent of Taft and Topsom[43]**

−R	$\Delta E_{IMHB(NO)}$	$\Delta E_{IMHB(O)}$	$\Delta E_{barrier}$	$\tilde{\nu}[1(n,\pi^*)^1]$	$\tilde{\nu}[1(\pi,\pi^*)^1]$	σ_{R^+}	σ_F	σ_α
$-NHCH_3$	18.33[a]	16.00[b]				−0.58	0.12	−0.30
$-NH_2$	17.73	15.42[b]	13.2	53.81	44.46	−0.52	0.14	−0.16
$-CH_3$	16.40	14.23	11.33	42.91	42.93	−0.08	0	−0.35
$-SCH_3$	14.58[a]	12.39[b]				−0.27	0.25	−0.68
−H	14.52	12.33	11.5	41.72	42.86	0	0	0
$-OCH_3$	14.47	12.28	17.6	55.28	44.46	−0.42	0.25	−0.17
−OH	14.36[a]	12.17[b]				−0.38	0.30	−0.03
−SH	14.14[a]	11.96[b]				−0.25	0.28	−0.55
−CN	13.01	10.97	11.94	41.15	40.01	0.00	0.60	−0.46
−F	12.07	10.13	19.28	54.99	43.89	−0.25	0.44	0.13
$-NO_2$	11.78	9.68	15.70	38.66	39.33	0.00	0.65	−0.26
−Cl	11.66	9.64	18.57	47.23	42.51	−0.17	0.45	−0.43

[a] Data from ref 33. [b] Values obtained by least-squares fitting of an $E_{IMHB(MO)}$ vs $E_{IMHB(O)}$ plot with $n = 7$ (−H, −Me, −OMe, −F, −Cl, −CN and $-NO_2$).

TABLE 3: Evaluation of Basicity and Acidity as the Energy Difference between Reactants and Products at the HF/6-31G Level in the Ground State and the CIS/6-31G**//HF/6-31G** Level in the $(n,\pi^*)^1$, $1(\pi,\pi^*)^1$, and $2(\pi,\pi^*)^1$ States (All Values in 10^3 cm^{-1})**

	ΔE
Benzaldehyde + $H^+ \rightarrow$ BenzaldehydeH$^+$	
S_0	−215.83
$1(\pi,\pi^*)^1$	−245.64
$1(n,\pi^*)^1$	−157.67
$2(\pi,\pi^*)^1$	−205.60
Phenol $\rightarrow$ Phenolate$^-$ + H^+	
S_0	373.87
$1(\pi,\pi^*)^1$	352.91

and acidity data for the phenol system in its ground and π,π^* excited states, which were computed at the HF/6-31G** and CIS/6-31G**//HF/6-31G** levels, respectively. These results can be used to construct the corresponding isodesmic processes:

$$\mathrm{phCOH}[1(\pi,\pi^*)] + \mathrm{phCOH_2}^+[S_0] \rightarrow \mathrm{phCOH_2}^+[1(\pi,\pi^*)] + \mathrm{phCOH}[S_0]$$
$$\Delta E = -29.8\ \mathrm{kcal/mol}$$

i.e., the basicity of the carbonyl oxygen in benzaldehyde increases by 29.8 kcal/mol from the ground state to the $1(\pi,\pi^*)$ state. On the other hand

$$\mathrm{phOH}[1(\pi,\pi^*)] + \mathrm{phO}^-[S_0] \rightarrow \mathrm{phO}^-[1(\pi,\pi^*)] + \mathrm{phOH}[S_0]$$
$$\Delta E = -20.9\ \mathrm{kcal/mol}$$

i.e., phenol is 20.9 kcal/mol more acidic in the excited electronic state that in the ground state.

Both energy differences between the two states are quite consistent with the results of Freiser and Beauchamp,[48] viz. −29 and −20 kcal/mol, respectively.

The corresponding isodesmic process for the basicity of benzaldehyde in its n,π^* will be

$$\mathrm{phCOH}[1(\pi,\pi^*)] + \mathrm{phCOH_2}^+[S_0] \rightarrow \mathrm{phCOH_2}^+[1(\pi,\pi^*)] + \mathrm{phCOH}[S_0]$$
$$\Delta E = +58.1\ \mathrm{kcal/mol}$$

so this state is 58 kcal/mol less basic than the ground state.

Consistent with the previous results, the ESIPT curve of the π,π^* type for 2-hydroxybenzaldehyde (−H) reflects the transfer, whereas that of the n,π^* type does not. Therefore, from the previous results it follows that all the 2-hydroxybenzoyl compounds studied here undergo proton transfer. However, none produces a zwitterionic form in the process since the molecular structure redistributes charges during the transfer and hinders the formation of a doubly charged structure in this aromatic system.

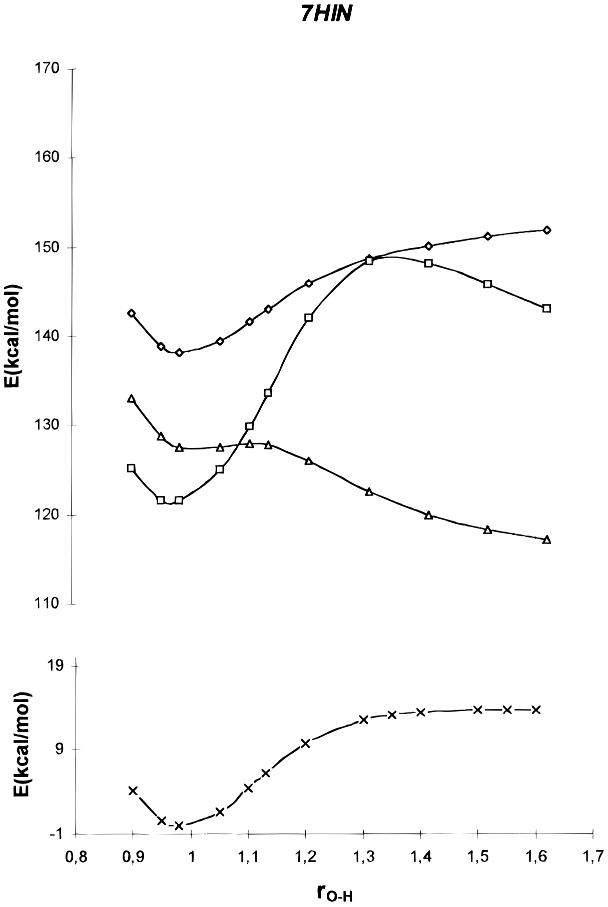


Figure 4. GSIPT curve (-×-) and $(n,\pi^*)^1$ (-□-), $1(\pi,\pi^*)^1$ (-△-), and $2(\pi,\pi^*)^1$ (-◇-) ESIPT curves of 7HIN constructed at the B3LYP/6-31G** and CIS/6-31G**+B3LYP/6-31G**//B3LYP/6-31G** levels, respectively. r_{O-H} in Å.

3.5. 7HIN. The molecular structure for this compound allows one to make some interesting comparisons with the 2-hydroxyacetophenone (−Me) geometry. On the one hand, its IMHB is weaker than that of −Me (9.89 vs 14.22 kcal/mol

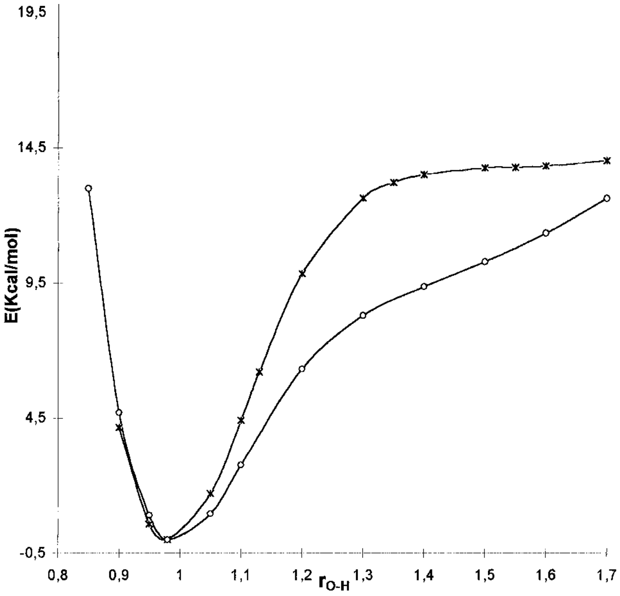


Figure 5. Comparison of the GSIPT curves for 2-hydroxyacetophenone (−Me) (○) and 7HIN (*) obtained at the B3LYP/6-31G** level. $r_{\mathrm{O-H}}$ in Å.

for $\Delta E_{\mathrm{IMHB(O)}}$); as a result, the length of the hydrogen bond is substantially longer in 7HIN ($r_{\mathrm{O-O}} = 2.805$ Å) than in −Me ($r_{\mathrm{O-O}} = 2.556$ Å), whereas $r_{\mathrm{O-H}}$ is shorter in the former than in the latter (0.983 vs 0.994 Å). In summary, the geometry obtained seemingly confirms the grounded predictions of Nagoaka et al.[16] regarding the effect of the presence of an ethylene bond on the structural characteristics of the compound. However, the predictions that the bond should give rise to a minimum in the transferred zone and thus to the first known double-minimum GSIPT curve for this type of compound fail utterly. In fact, based on the theoretical B3LYP/6-31G** results (Figure 4), the GSIPT curve for this compound contains a single minimum that is located in the enol zone. It is true, however, that the ethylene bond in this compound increases the instability of the transferred zone relative to 2-hydroxyacetophenone (see Figure 5). Nevertheless, we should note that, for the first time, a curve preserves its instability beyond its midpoint and forms a plateau that will no doubt hinder the return a structure of this type in the ground electronic state to the energy minimum for the nontransferred zone. One other special feature is that, despite the presence of the ethylene bond, the oxygen atoms approach significantly halfway through the proton transfer in 7HIN [$r_{\mathrm{O-H}} = 0.983$ Å ($r_{\mathrm{O-O}} = 2.805$ Å), $r_{\mathrm{O-H}} = 1.35$ Å ($r_{\mathrm{O-O}} = 2.457$ Å), and $r_{\mathrm{O-H}} = 1.7$ Å ($r_{\mathrm{O-O}} = 2.630$ Å)].

The corresponding ESIPT curves for 7HIN (Figure 4) are also consistent with experimental evidence. Thus, the first π,π^* state produces an ESIPT curve with a minimum in the transferred zone. This curve also appears to have an incipient minimum in the enol zone, with a very low barrier to the proton transfer (about 0.5 kcal/mol). The presence of this potential enol minimum in the ESIPT curve for the π,π^* state is of lesser photophysical significance because the n,π^* singlet is more stable in this zone. This last situation is consistent with the predictions of Nagoaka et al.[16] and Chow[19] in that the first n,π^* and π,π^* states for this compound must be energetically close.

4. Conclusions

The B3LYP/6-31G** results for the proton transfer of 2-hydroxybenzoyl compounds in the ground electronic state provide a curve with a single minimum in the enol zone where structures evolve from a typical enol form to the keto form by an approach of the atoms that bear the IMHB in the midpoint of the transfer.

The ESIPT curves constructed as CIS/6-31G** Franck−Condon curves from B3LYP/6-31G** GSIPT curves exhibit a $1(\pi,\pi^*)^1$ state that is responsible for the proton transfer in the excited state, with a potential curve containing a single minimum (in the transferred zone), in addition to a $(n,\pi^*)^1$ state with a double-minimum curve made unstable in the transferred zone. It should be noted that the potential barrier to the proton transfer in the $1(\pi,\pi^*)^1$ state disappears on introducing electronic correlation for the ground state.

Taft's parametric model for the substituent effects describes the different dependences of the hydrogen bond strength and energy barrier for the proton transfer on the substituent since it predicts that these two parameters are unrelated.

This model also describes the energies of transition to the $1(\pi,\pi^*)^1$ and $(\mathrm{n},\pi^*)^1$ states for these compounds; the $(\mathrm{n},\pi^*)^1$ state is strongly shifted hypsochromically as the substituent resonance increases. This is why the enol form possesses n,π^* connotations in the first excited state only in those compounds with a nonresonant −R.

All the results obtained in this work suggest that the transfer process is a proton transfer in the $1(\pi,\pi^*)^1$ state, which, however, involves no zwitterionic structure.

The presence of an ethylene bond in 7HIN considerably weakens the hydrogen bond in this species. However, it does not give rise to a double minimum for the transfer in the ground state. On the other hand, the source of instability in the transferred zone is indeed preserved and appears as a plateau in the GSIPT curve.

All these theoretical results are quite consistent with photophysical experimental evidence for this type of compound and contribute information on the nature of the processes involved.

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Supporting Information Available: Ground-state energies (B3LYP/6-31G**) and IMHB system distances for the GSIPT curves and excitation energies (CIS/6-31G**) for the ESIPT curves of 2-hydroxybenzoyl compounds (6 pages). Ordering information is given on any current masthead page.

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