# Theoretical Evaluation of Solvent Effects on the Conformational and Tautomeric Equilibria of 2-(2′-Hydroxyphenyl)benzimidazole and on Its Absorption and Fluorescence Spectra

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*Received: December 17, 1998*

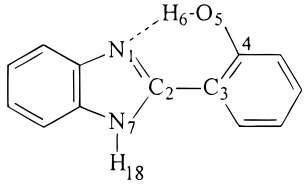
The effect of the solvent on the ground state free energy differences of three enol conformers of 2-(2′-hydroxyphenyl)benzimidazole and its keto tautomer has been examined by means of Monte Carlo simulations and continuum model calculations. In agreement with the experimental data, calculations show that the trans enol and keto forms are stabilized by polar solvents, leading to a conformational and tautomeric equilibrium with the closed cis enol conformer in water, the only single species in apolar solvents. Monte Carlo simulations have also been used to examine the influence of the solvent on the absorption band of the closed cis enol structure and the fluorescence band of the keto form generated by photoinduced intramolecular proton transfer. In concordance with the experimental spectra, absorption and fluorescence band maxima for the closed cis enol and keto forms, respectively, are found to be blue-shifted with increasing polarity and hydrogen bonding capacity of the solvent.

## Introduction

The molecule 2-(2′-hydroxyphenyl)benzimidazole (HPBI, Scheme 1) is characterized by having a proton donor (−OH) group and a proton acceptor (−N═) site connected by an intramolecular hydrogen bond in the ground state. When this molecule is photoexcited, there is an electronic charge redistribution that enhances the acidity and basicity of the proton donor and proton acceptor groups, respectively. As a consequence, the hydrogen atom is transferred from the acidic center to the basic group via an ultrafast excited state intramolecular proton transfer (ESIPT) process.[1,2] This elementary, but very important reaction, has also been observed in a number of other compounds containing proton donor (−OH, $-NH_2$) and proton acceptor (−N═, −C═O) groups connected by an intramolecular hydrogen bond in the ground state.[3−13] These molecules are the object of current interest because of their utility as polymer ultraviolet stabilizers[3,14−16] and laser dyes,[7,17−21] as well as for their implications in biology and potential applications as molecular switches in logic or memory circuits.[22]

HPBI may exist in three different enol conformers and a keto tautomeric structure (Figure 1). It is generally accepted[3−5,23−25] that in the ground state the closed cis enol species, which is characterized by the N···HO intramolecular hydrogen bond, is the only form present in apolar or low polar solvents. Nevertheless, the stability of the closed cis enol conformer relative to the other species is substantially reduced as the hydrogen bonding ability of the solvent increases.[3,4,23,26,27] In this case, there is a controversy whether the open cis enol[4,7] or the trans enol[3,5,26,27] structure (see Figure 1) is in equilibrium with the closed cis enol form. Finally, in very polar solvents the keto form has also been detected in equilibrium with the closed cis enol.[26]

**SCHEME 1**




HPBI

HPBI exhibits a rich photochemistry that varies with solvent polarity and hydrogen bonding capacity.[3−5,7,23−28] The absorption spectrum of HPBI shows four bands at about 330, 280, 260, and 220 nm, the exact position of each band depending on the nature of the solvent.[4] The long wavelength absorption band maximum is attributed to the presence of the closed cis enol form and is slightly blue-shifted with increasing polarity and proton donor/acceptor ability of the solvent. In all solvents, the photoexcitation of the closed cis enol form involves an ESIPT to form the phototautomer, which yields a large Stokes-shifted emission. Further, in polar protic solvents dual fluorescence is observed. Apart from the aforementioned keto fluorescence, the open cis enol or trans enol form (different opinions exist as commented before) produces a normal Stokes-shifted

10.1021/jp984773+ CCC: $18.00 
Published on Web 05/25/1999

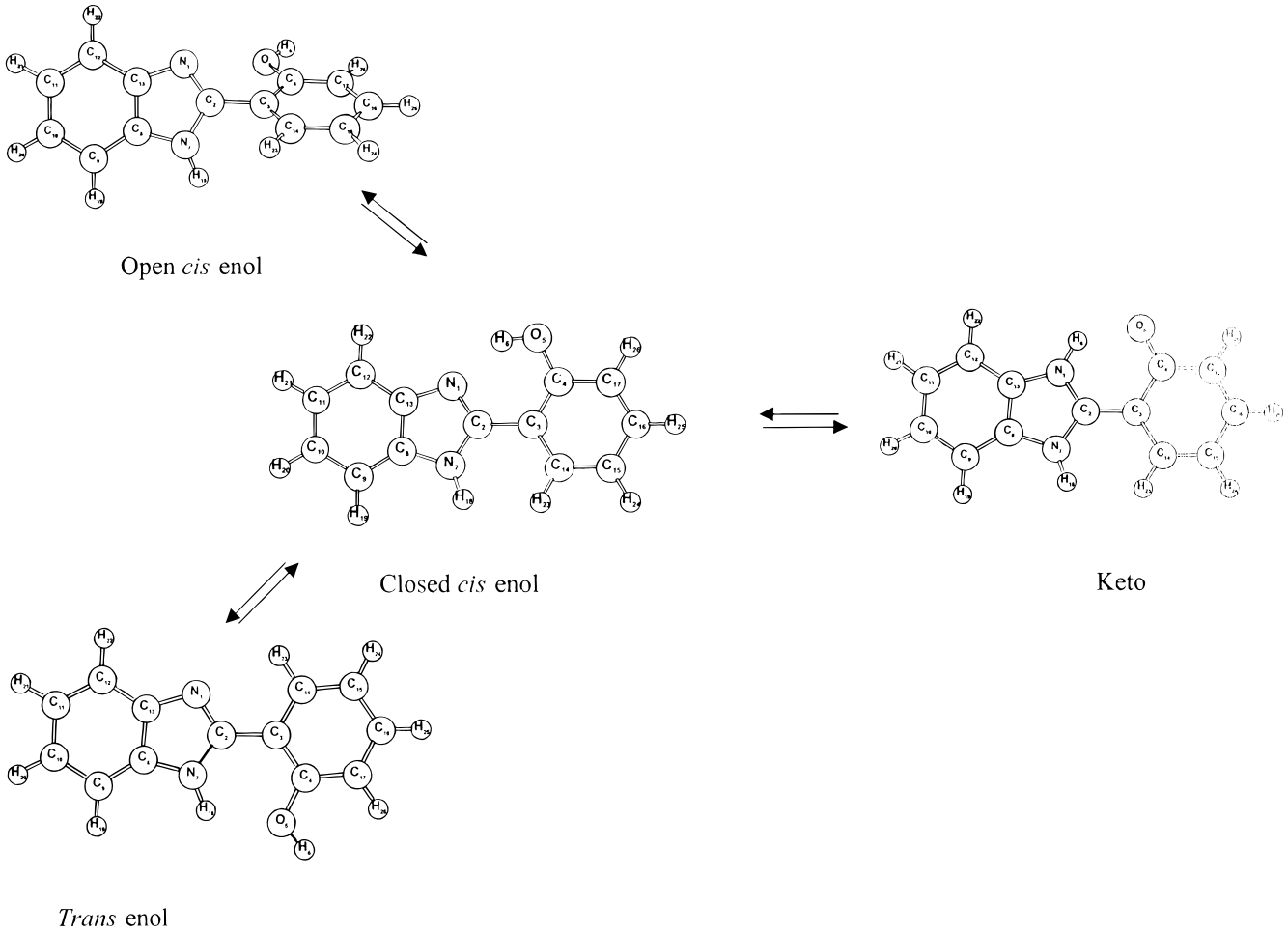



**Figure 1.** The optimized structures of the three enol conformers of 2-(2′-hydroxyphenyl)benzimidazole and its keto tautomeric form in the ground state.

fluorescence after its photoexcitation.[5] The low energy fluorescence band is largely blue-shifted with increasing polarity and hydrogen bonding capacity of the solvent, while the normal Stokes-shifted band is slightly red-shifted in water as compared to methanol.[4] Moreover, in hydrogen bonding solvents, the intensity of the large Stokes-shifted fluorescence band is further reduced because of the formation of intermolecular hydrogen bonds that inhibit the ESIPT process in HPBI.[3,4,23,26,27] As one can see, the nature of the solvent plays an important role, both on the conformational and tautomeric equilibria[26] and on the absorption and fluorescence spectra of HPBI.[4,7]

Ab initio studies dealing with HPBI have been concentrated basically on the study of the gas phase first singlet $^1\pi\pi^*$ ESIPT process in model systems.[29−32] Theoretically, the solvent effect on the $^1\pi\pi^*$ ESIPT process of HPBI has been usually taken into account semiempirically.[3−5] Recently, Ríos and Ríos[32] have reported ab initio HF/3-21G* and CIS/3-21G* calculations to discuss the solvent effects on the intramolecular proton transfer in the ground and first excited states of HPBI by means of continuum and specific models. However, in their work the effect of the environment on the ground state conformational equilibrium has not been examined.

The present investigation addresses the preceding point, *i.e.*, how the nature of the solvent can modulate the relative stability of the different rotamers and tautomers of HPBI, which in turn determines the nature of the photoinduced proton transfer processes that take place in the excited state. In addition, our interest is also focused on the solvent-induced shifts in absorption and fluorescence spectra of HPBI, which to the best of our knowledge have not yet been considered in previous theoretical studies. The results reported here provide new clues for understanding the particular behavior of HPBI.

## Computational Details

All geometries in the ground state were fully optimized at the restricted Hartree−Fock (HF) level. The minimum energy nature of the stationary points was verified from vibrational frequency analysis. To estimate the contribution of electron correlation effects, single point energy calculations were performed with the density functional hybrid B3LYP method, which employs Becke's three-parameter exchange functional[33] and the Lee−Yang−Parr nonlocal correlation functional.[34] The double-ζ Gaussian basis set of Dunning and Hay with polarization functions (D95**)[35] was employed in the calculations performed at the HF and B3LYP levels. In addition, B3LYP calculations were also carried out with the D95++** basis set in order to examine the influence of basis set extension on the results. The thermodynamics in gas phase was computed by correcting the differences in electronic energy to enthalpies at 298 K upon inclusion of zero-point energy and thermal corrections. The free energy differences were estimated from the addition of entropy corrections. Zero-point energy and thermal and entropy corrections were determined following the standard procedures in GAUSSIAN 94.[36] The closed cis enol, trans enol, and keto forms were also fully optimized in the $^1\pi\pi^*$ excited state using the configuration interaction with single excitation (CIS) procedure[37] and the D95** basis set. Core electrons were not correlated in the CIS calculations.

The influence of solvation on the stability of the ground-state structures was examined by using Monte Carlo free energy perturbation (MC-FEP) and self-consistent reaction field (SCRF) methods. To examine the solvent effect on the relative stability between enol and keto forms of HPBI, calculations were performed in water and in chloroform.

MC-FEP simulations were carried out to compute the difference in solvation free energy ($G_{sol}$) of the open cis enol, trans enol, and keto structures with respect to the closed cis enol species. Particularly, the relative free energies of solvation were determined from the reversible work spent in mutating this latter form into the other rotamer/tautomer form in solution. Mutations were performed using the windowing scheme. A total of 21 double-sampling windows were considered in the simulation. Each window involved two- and three-million configurations for equilibration and averaging, respectively. Preferential sampling was utilized to improve the statistics around the solute. Simulations were carried out in the isothermal−isobaric ensemble at a temperature of 298 K and 1 atm of pressure using periodic boundary conditions. Changes in volume and solute translations and rotations were adjusted to obtain around 40% acceptance. The simulation systems consisted of one solute embedded in around 500 TIP4P[38] water or 125 chloroform[39] molecules. The van der Waals parameters were taken from the OPLS[40] force field, and the atomic partial charges were determined from fitting to the electrostatic potential[41,42] computed at the HF/D95** level. A cutoff of 8 Å was used in simulations. Test calculations revealed no significant changes in the relative free energies of solvation when larger cutoffs were considered.

SCRF calculations were performed using the MST model,[43] also known as the polarizable continuum model.[44] In SCRF calculations, the relative free energies of solvation are determined from the difference between the free energies of solvation of the open cis enol, trans enol, and keto structures with respect to that of the closed cis enol species. Computations were carried out with our optimized semiempirical AM1[45] and ab initio HF/6-31G*[46] versions.[43]

The study of the solvent effect on electronic transitions was performed for six different solvents, which besides water and chloroform include methanol, acetonitrile, acetone, and carbon tetrachloride. On the basis of the Franck−Condon principle, it has been considered that vertical transitions alter the charge distribution of the solute but not its geometry. As far as the solvent molecules are concerned, the extreme speed of the photoexcitation precludes any large-scale solvent reorganization during the process.[2] Following previous studies,[47] the effect of solvation on the vertical electronic transitions was examined by using MC-FEP simulations, which involved mutations of the solute charge distribution for the ground and excited states in just one step. During these simulations the solvent equilibrates with the reference state of the solute, i.e., the ground state in an absorption process, and the mutated state "fits" into the cage structure of solvent molecules adapted to the reference solute, thus modeling the Franck−Condon principle. Therefore, in one-window MC-FEP simulations of the vertical transitions the charge distribution in HPBI is allowed to change, but both its geometry and the position of the water molecules are kept frozen. At every MC step, the difference in interaction energy between ground and excited states with the solvent molecules was subsequently calculated and averaged over the entire trajectory to estimate the solvent frequency shift. It must be noted, nevertheless, that this procedure neglects the contribution due to the instantaneous electronic polarization. These calculations were carried out in the isothermal−isobaric ensemble (298 K, 1 atm), and the simulation systems consisted of the ground state closed cis enol and excited state keto tautomers inmersed in around 500 (TIP4P water), 260 (methanol, dimethyl ether, acetonitrile), or 125 (chloroform, carbon tetrachloride) solvent molecules. Electrostatic potential derived charges were utilized to represent the ground and excited state charge distribution of the solute. A cutoff of 8 Å was used in simulations. Test calculations performed in water with a cutoff of 9 Å showed no relevant differences in the results.

All geometry optimizations and single point energy evaluations were performed with the GAUSSIAN 94[36] program. MC-FEP simulations were carried out using the BOSS molecular simulation program.[48] SCRF calculations were performed using locally modified versions of Monstergauss and MOPAC computer programs. All calculations were done in an IBM-PS2 computer of the Centre de Supercomputació de Catalunya (CESCA) and on workstations in our laboratory.

**TABLE 1: Gas Phase Differences in Internal Energy, Enthalpy, and Free Energy (kcal mol$^{-1}$) between Enol and Keto Forms of 2-(2′-Hydroxyphenyl)benzimidazole[a] together with Their $C_2C_3$ Bond Length (in Å) in the Ground State Determined from HF and B3LYP Calculations with the D95** Basis Set**

| molecule | $\Delta E$ | $\Delta H°$ | $\Delta G°$ | $C_2C_3$ |
|---|---|---|---|---|
| closed cis enol | | | | |
| HF | 0.0 | 0.0 | 0.0 | 1.472 |
| B3LYP[b] | 0.0 | 0.0 | 0.0 | |
| | *0.0* | *0.0* | *0.0* | |
| open cis enol | | | | |
| HF | 11.2 | 10.7 | 9.8 | 1.480 |
| B3LYP | 14.2 | 13.7 | 12.8 | |
| | *13.9* | *13.4* | *12.5* | |
| trans enol | | | | |
| HF | 4.2 | 4.0 | 4.0 | 1.484 |
| B3LYP | 6.4 | 6.2 | 6.2 | |
| | *5.9* | *5.7* | *5.7* | |
| keto | | | | |
| HF | 13.1 | 12.5 | 12.8 | 1.413 |
| B3LYP | 10.6 | 10.0 | 10.3 | |
| | *10.3* | *9.7* | *10.0* | |

[a] The notation used for the enol species denotes the conformations corresponding to the rotation around the $C_2C_3$ bond. See Figure 1. [b] Results determined from single point B3LYP/D95++** calculations using the HF/D95** optimized geometries are given in italics. Total energies for the ground-state closed cis enol form are −682.026455, −686.260934, and −686.278163 hartrees at the HF/D95**, B3LYP/D95**//HF/D95**, and B3LYP/D95++**//HF/D95** levels. Zero-point energies and thermal and entropy corrections determined at the HF/D95** level.

## Results and Discussion

**Ground State Conformational and Tautomeric Equilibria.** The three different conformational isomers of HPBI and its tautomeric keto form optimized in the ground state are displayed in Figure 1. The open cis enol form is obtained from the closed cis enol structure through rotation of the $C_3C_4O_5H_6$ and $N_1C_2C_3C_4$ dihedral angles by 180° and 59.4°, respectively. Starting from the open cis enol form, the trans enol structure is reached by increasing the $N_1C_2C_3C_4$ dihedral angle to 180°. The ground state energy differences in gas phase between the closed cis enol structure and the other forms, as well as the $C_2C_3$ bond distance for each form, have been compiled in Table 1.

As found experimentally, the results obtained from HF and B3LYP calculations indicate clearly that the closed cis enol form is the most stable form in the ground state,[3−5,23−25] the energy difference with regard to the other species being larger than 4

**TABLE 2: Relative Free Energies of Solvation (kcal mol$^{-1}$) in Water and Chloroform for the Ground-State Enol and Keto Forms of 2-(2′-Hydroxyphenyl)benzimidazole Determined from MST-AM1, MST-HF/6-31G*, and MC-FEP Calculations**

| molecule | MST-AM1[a] | MST-HF/6-31G*[a] | MC-FEP |
|---|---|---|---|
| water | | | |
| closed cis enol | 0.0 (−8.2) | 0.0 (−6.5) | 0.0 |
| open cis enol | −7.3 (−15.5) | −6.6 (−13.1) | −4.3 |
| trans enol | −2.4 (−10.6) | −2.1 (−8.6) | −4.6 |
| keto | −6.3 (−14.5) | −6.6 (−13.1) | −12.6 |
| chloroform | | | |
| closed cis enol | 0.0 (−14.2) | 0.0 (−15.0) | 0.0 |
| open cis enol | −1.7 (−15.9) | −2.3 (−17.3) | −1.0 |
| trans enol | −0.8 (−15.0) | 0.0 (−15.0) | −0.6 |
| keto | −1.8 (−16.0) | −2.4 (−17.4) | −1.7 |

[a] Absolute free energies of solvation are given in parentheses.

kcal mol$^{-1}$. Comparison of HF and B3LYP results reveal that inclusion of electron correlation effects increases the destabilization of the open cis enol and trans enol rotamers by 2−3 kcal mol$^{-1}$ with regard to the closed cis enol species, whereas the keto structure is stabilized by 2.5 kcal mol$^{-1}$. These changes, nevertheless, do not alter substantially the ordering of the relative energies for the different rotamers and tautomers, with the only exception being the open cis enol and keto species, since the former becomes less favored than the keto structure by more than 3 kcal mol$^{-1}$ at the B3LYP level. On the other hand, extension of the basis set by addition of diffuse functions to the D95** basis set leads to very small changes in the relative stabilities. Results in Table 1 also show that the relative stability of the different forms in the gas phase does not change significantly after inclusion of zero-point energies and thermal and entropy corrections. Accordingly, the results allow us to state the following ordering of stability in the gas phase ground state: closed cis enol, trans enol, keto, and finally open cis enol.

The larger stability (5.7 kcal mol$^{-1}$ at the B3LYP/D95++** level) of the closed cis enol form with respect to the trans enol conformer can be attributed to the stronger $O_5H_6\cdots N_1$ hydrogen bond as compared to the $O_5\cdots H_{18}N_7$ hydrogen bond, which results from the better proton donating ability of O and accepting capacity of N. The same behavior was found in model systems of 2-(2′-hydroxyphenyl)benzoxazole (HPBO)[49] and HPBI.[30] The large destabilization of the open cis enol form in comparison to the closed cis enol conformer (by 13.9 kcal mol$^{-1}$ at the B3LYP/D95++** level) is mostly due to the breaking of the intramolecular hydrogen bond and the loss of delocalization, which are not compensated by the stabilization coming from the reduction in Pauling repulsions. Finally, the loss of aromaticity of the phenol ring is the main reason[29] to explain the minor stability of the keto form (by 10 kcal mol$^{-1}$ at the B3LYP/D95++** level) with respect to the closed cis enol form. The difference between the longest and shortest C−C bond distances in the ring is 0.027 Å for the closed cis enol form and 0.100 Å for the keto form, indicating a larger aromaticity in the phenol ring of the closed cis enol form.[50] It is worth noting here the notable shortening of the $C_2C_3$ bond upon conversion of the closed cis enol to the keto structure, as expected from the increased partial double bond character of the $C_2C_3$ bond in the latter tautomer.

The free energies of solvation in chloroform and water of the different species in the ground state determined from MST-AM1 and MST-HF/6-31G* calculations are gathered in Table 2. There is agreement between the absolute free energies of solvation computed at both MST-AM1 and MST-HF/6-31G* levels in the two solvents. The results in Table 2 indicate that there are small differences in the free energy of solvation of the enol and keto species in chloroform. Thus, even though the closed cis enol species is the less favored form upon solvation, the difference with regard to the other structures is less than or around 2 kcal mol$^{-1}$. Nevertheless, there are relevant differences in the stabilization of the different species upon solvation in water, where hydration stabilizes preferentially the keto and open cis enol species with regard to the trans enol, which in turn is better hydrated than the closed cis enol structure. With exception of the open cis enol rotamer, the preferential hydration roughly follows the differences in the polarity of enol and keto forms, as noted in the gas phase dipole moments, which are 4.0 (closed cis enol), 4.2 (open cis enol), 5.0 (trans enol), and 6.3 (keto) Debyes at the HF/D95** level. The larger stabilization of the open cis enol with regard to the closed cis and trans enol structures can be realized from the breaking of the intramolecular hydrogen bond, which leads in turn to a more intense interaction with the polarizable dielectric.

The differences in free energy of solvation obtained from MC-FEP simulations are also given in Table 2. Comparison of MST and MC-FEP results shows close agreement between the relative free energies of solvation in chloroform. Thus, the closed cis enol is the less stabilized form upon solvation, but the difference with regard to the other species is less than 2 kcal mol$^{-1}$. In water there is also qualitative agreement between MST and MC-FEP results, since the open cis enol, trans enol, and keto forms are sensibly more stabilized than the closed cis enol. However, there are some quantitative differences in the relative hydration-free energies determined from the two methods, especially in the case of the keto tautomer, since the MC-FEP estimated is found to be around 6 kcal mol$^{-1}$ (in absolute value) larger than the MST one. The origin of this discrepancy, which is particularly large in view of the general agreement found between MST and MC-FEP methods for the solvation of other molecular systems,[51] is not clear and deserves further study. However, comparison with the available experimental data (see below) allows us to speculate that a too simple description of the solute/solvent interface in MST calculations,[52,53] and the involvement of strong specific interactions of water molecules with HPBI, which cannot be properly dealt with in SCRF calculations, might contribute to explain such a difference. It is worth mentioning that a recent study on the ground state tautomerism and rotamerism of 4,5-dimethyl-2-(2′-hydroxyphenyl)imidazole (DMHPI) in solution has revealed that specific water−solute interactions are very important to account for the differential solvation of the different isomers.[54]

Table 3 gives the free energy differences in water and chloroform of the open cis enol, trans enol, and keto species relative to the closed cis enol form. These values were determined by adding the relative free energies of solvation computed from MST and MC-FEP simulations to the free energy differences in the gas phase calculated from HF and B3LYP calculations (Table 1). Inspection of the results in Table 3 shows that the closed cis enol is the only species predicted to exist in chloroform solution, since the difference with regard to the other enol and keto species is at least larger than 3 kcal mol$^{-1}$. This finding is in agreement with the available experimental evidence, which indicates that the only detectable species in apolar or low polar solvents is the closed cis enol.[3−5,23−25]

The conclusions for the equilibrium between rotamers and tautomers in aqueous solution are different depending on whether the MST or MC-FEP relative free energies of solvation are considered (see above). In the former case the closed cis enol is predicted to be the main species, the other structures

**TABLE 3: Free Energy Differences[a] (kcal mol$^{-1}$) in Water and Chloroform for the Ground-State Enol and Keto Forms of 2-(2′-Hydroxyphenyl)benzimidazole**

| molecule | | MST[b] | MC-FEP |
|---|---|---|---|
| water | | | |
| closed cis enol | HF | 0.0 | 0.0 |
| | B3LYP | 0.0 | 0.0 |
| | | *0.0* | *0.0* |
| open cis enol | HF | 2.8 | 5.5 |
| | B3LYP | 5.8 | 8.5 |
| | | *5.5* | *8.2* |
| trans enol | HF | 1.7 | −0.6 |
| | B3LYP | 3.9 | 1.6 |
| | | *3.4* | *1.1* |
| keto | HF | 6.3 | 0.2 |
| | B3LYP | 3.8 | −2.3 |
| | | *3.5* | *−2.6* |
| chloroform | | | |
| closed cis enol | HF | 0.0 | 0.0 |
| | B3LYP | 0.0 | 0.0 |
| | | *0.0* | *0.0* |
| open cis enol | HF | 7.8 | 8.8 |
| | B3LYP | 10.8 | 11.8 |
| | | *10.5* | *11.5* |
| trans enol | HF | 3.6 | 3.4 |
| | B3LYP | 5.8 | 5.6 |
| | | *5.3* | *5.1* |
| keto | HF | 10.7 | 11.1 |
| | B3LYP | 8.2 | 8.6 |
| | | *7.9* | *8.3* |

[a] Values determined from addition of the relative free energy differences in gas phase computed at the HF and B3LYP levels to the relative free energies of solvation determined from MST and MC-FEP simulations. The results obtained from the free energy differences computed at the B3LYP/D95++** level are given in italics. [b] The relative free energy of solvation has been determined as the average of the MST-AM1 and MST-HF/6-31G* values.

being destabilized by at least 1.7 kcal mol$^{-1}$. A more complex rotameric and tautomeric equilibrium between the closed cis enol, trans enol, and the keto structures is predicted when the MC-FEP results are considered. Regarding the enol conformers, even though the results allow us to rule out a significant population of the open cis enol form, the stability of the closed cis enol and trans enol forms is found to be comparable. There is evidence from previous theoretical calculations on HPBI and related species indicating that the equilibrium between these two conformers can be easily reached. In particular, CNDO/S-CI calculations performed at the ground state AM1 optimized geometries by Das et al.[3] yielded an energy barrier for the isomerization of the ground state closed cis enol form of HBPI to the trans enol structure of 4.1 kcal mol$^{-1}$. This barrier is reduced by 0.9 kcal mol$^{-1}$ when the effect of an ethanol solution is included in the calculation. Moreover, HF/D95** calculations on model systems of HPBI indicated that this barrier is ca. 8 kcal mol$^{-1}$ in the gas phase.[30] Finally, for a related molecule, 2-(2′-hydroxyphenyl)oxazole (HPO), Guallar et al.[49] found that the barrier for the conversion of the closed cis enol form to the trans enol conformer is 11.7 kcal mol$^{-1}$ at the HF/6-31G* level. Furthermore, we expect a reduction of this barrier in water, on the basis of the calculations by Das et al.[3] in solution and on the larger stabilization of the trans enol conformer compared to the close cis enol form in water (Table 2). Thus, one can reasonably assume a conformational equilibrium between these two conformers at room temperature. This conclusion agrees with the experimental finding that the trans enol conformer is in equilibrium with the closed cis enol form in ethanol solution.[3,5,26,27] Moreover, the analysis of the spectra of the bridged HPBI,[55] a system fixed in the cis conformation, led to suggest the existence of an equilibrium between the closed cis enol and the trans enol structures in polar solvents. Finally, the existence of the trans enol species in alcohol solutions has also been observed for closely related structures, like 2-(2′-aminophenyl)benzimidazole (APBI), the amino version of HPBI.[56]

According to the results in Table 3, the stability of the keto tautomer is predicted to be similar or even larger than that of the closed cis enol form in water. Even though we have not attempted to compute the energy barrier for this intramolecular proton transfer, there is experimental and theoretical evidence supporting the existence of an equilibrium between the keto and closed cis enol forms. From a theoretical point of view, HF/3-21G* calculations by Ríos and Ríos[32] yielded an energy barrier for the proton transfer that converts the closed cis enol form of HPBI to the keto tautomer of 9.5 kcal mol$^{-1}$ in the gas phase and of 6.6 kcal mol$^{-1}$ in water. For model systems of HPBI, the energy barrier for the gas phase proton transfer process in the ground state ranges from 8.7 to 17.6 kcal mol$^{-1}$.[30] The corresponding barrier for DMHPI is 13.8 kcal mol$^{-1}$ at the HF/6-31+G* level.[54] Inclusion of correlation energy should lower these barriers.[29,30,49,50] Also, the larger stabilization of the keto form as compared to the closed cis enol tautomer in water should reduce the barrier. Therefore, we expect the existence of an equilibrium between these two forms in water. Experimentally, the keto form has been found to be in equilibrium with the closed cis enol form in water, with an estimated equilibrium constant of 0.1.[26] Moreover, similar findings have been reported for related compounds, such as 2-(3′-hydroxy-2′-pyridyl)benzimidazole (HPyBI).[57]

Comparison of the results given in Tables 1 and 3 shows the remarkable influence of solvation on the conformational and tautomeric equilibria of HPBI. In apolar or low polar solvents, the intrinsic gas phase stability controls the relative weight of the different rotamers and tautomers, favoring the existence of the intramolecularly hydrogen bond closed cis enol. Solvation in polar, protic solvents stabilizes preferentially the keto, open cis enol, and trans enol forms with regard to the closed cis enol species, and for the particular case of water the keto and trans enol structures are predicted to be in equilibrium with the closed cis enol form. Recently, it has been shown that this equilibrium can be greatly altered by introduction of appropriate substituents.[54,58] Thus, the 1-methyl derivative of HPBI has been reported to exist only as the nonplanar enol form,[58] and only an equilibrium between the keto and trans enol tautomers has been observed for DMHPI in aqueous solution.[54] Finally, for HPyBI[57] the keto form was found to exist in comparable amounts to the cis enol form in neutral aqueous solution. These studies, in conjunction with the results presented here, show that solvent and substituents can be exploited to control the predominant ground state rotamer/tautomer, and subsequently they are key factors for determining the nature of photoinduced proton transfer processes.

**Absorption and Fluorescence Spectra.** The gas phase energy differences between the closed cis enol and the trans enol and keto forms in the $^1\pi\pi^*$ excited state are given in Table 4, which also shows the corresponding $C_2C_3$ bond distance for the optimized geometries in the excited state. In view of the preceding results and the available experimental data, the open cis enol form has not been considered given its low stability in the ground state that translates into an insignificant influence on the absorption and fluorescence spectra.

Results in Table 4 show that in the $^1\pi\pi^*$ excited state the keto form is the most stable species. As compared to the closed cis enol conformer, the keto structure is more stable by 3.2 kcal mol$^{-1}$ at the CIS/D95** level (such a preference has been

**TABLE 4: Gas Phase Differences in Internal Energy (kcal mol$^{-1}$) between the Closed Cis Enol, Trans Enol, and Keto Forms of 2-(2′-Hydroxyphenyl)benzimidazole and Their $C_2C_3$ Bond Length (in Å) in the $^1\pi\pi^*$ Excited State Computed at the CIS/D95** Level**

| molecule | $\Delta E$ | $C_2C_3$ |
|---|---|---|
| closed cis enol | 0.0[a] | 1.398 |
| trans enol | 3.7 | 1.400 |
| keto | −3.2 | 1.409 |

[a] The total energy for the CIS/D95** optimized closed cis enol structure is -681.848766 hartrees in the $^1\pi\pi^*$ excited state.

determined to be 10.0 and 7 kcal mol$^{-1}$ from CIS/3-21G*[32] and CNDO/S-CI[3] calculations, respectively). The keto form was also found to be the most stable structure in the first excited state of related compounds, such as HPO,[49] benzoxazole,[3] HPyBI,[57] and APBI.[56] The electronic redistribution that takes place after the $^1\pi\pi^*$ photoexcitation is responsible for the switch in the relative stability of the two tautomers.[30] Therefore, after photoexcitation of the closed cis enol form, a tautomerization process is expected to occur via an ESIPT process.

Analysis of the geometrical changes shows that upon electronic excitation the enol structure experiences a loss of aromaticity (mainly in the phenol ring, where the difference between the longest and the shortest C−C bond distances in the ring is increased by 0.027 Å) that diminishes its stability. On the other hand, according to the bond distances, the aromaticity in the ring of the keto form in the $^1\pi\pi^*$ excited state is nearly the same as in the ground state. Similar findings have been reported in ab initio studies of HPBI model systems.[29,30] Likewise, CNDO/S-CI semiempirical results for HPBI also indicated a lower stability for the keto form with respect to the closed cis enol species in the ground state and a switch of the relative stability between these two forms in the excited state.[3,5] As stated for the closed cis enol form, the phenol ring of the trans enol structure undergoes a loss of aromaticity in the $^1\pi\pi^*$ transition (the difference between the longest and the shortest C−C bond distances in the ring is increased by 0.058 Å), and, as a consequence, the relative stability of the closed cis and trans enol forms are similar in the ground state and in the $^1\pi\pi^*$ excited state.

The gas phase adiabatic excitation energy for the closed cis enol conformer is 115.5 kcal mol$^{-1}$, and its gas phase vertical excitation energy is 120.1 kcal mol$^{-1}$ at the HF−CIS/D95** level of theory. This latter estimate is larger than the experimental value in cyclohexane by 34.8 kcal mol$^{-1}$.[4] This is not completely surprising taking into account that errors in vertical and adiabatic CIS singlet excitation energies larger than 1 eV are not unusual.[59−61]

Table 5 lists the solvent contributions determined from MC-FEP simulations to the electronic transition from the ground to the first excited state of the closed cis enol form in different solvents. On the basis of the results of the previous section, the MC-FEP method has been preferred over the MST procedure to introduce the solvent effects on the absorption and fluorescence band maxima. Upon inspection of the values in Table 5 one can notice that the solvent contribution for the closed cis enol $S_0 \rightarrow {}^1\pi\pi^*$ transition slightly increases with the permittivity of the solvent. Thus, in agreement with the experimental data,[4] the absorption band maximum gets slightly blue-shifted in polar solvents, which is usually consistent with a charge transfer transition leading to an excited state of reduced polarity,[62,63] as noted in the vertical dipole moments of the closed cis enol form in the ground state (3.98 D) and the first excited state (3.45 D).[64] Also, the relatively small difference in the two computed

**TABLE 5: Differential Solvation Contributions (kcal mol$^{-1}$) to the Vertical Electronic Transitions $S_o \rightarrow {}^1\pi\pi^*$ in the Closed Cis Enol Form and $^1\pi\pi^* \rightarrow S_o$ in the Keto Tautomer Determined from MC-FEP Simulations**

| solvent | $\epsilon$[a] | closed cis enol[b] $S_o \rightarrow {}^1\pi\pi^*$ | keto[c] $^1\pi\pi^* \rightarrow S_o$ |
|---|---|---|---|
| $H_2O$ | 78.4 | 1.0 | −6.7 |
| $CH_3CN$ | 35.9 | 1.1 | −3.1 |
| $CH_3OH$ | 24.6 | 1.2 | −4.9 |
| $CH_3OCH_3$ | 5.2 | 1.0 | −2.6 |
| $CHCl_3$ | 4.8 | 0.4 | −1.6 |
| $CCl_4$ | 2.2 | 0.0 | −0.1 |

[a] Permittivity of the solvent. [b] The HF/D95** optimized geometry of the closed cis enol form in the ground state $S_o$ was used in calculations. The state of reference is $S_o$. Positive values indicate a larger stabilization of the $S_o$ as compared to the $^1\pi\pi^*$ state, and consequently a blue-shifted absorption. [c] The CIS/D95** optimized geometry of the keto form in the $^1\pi\pi^*$ excited state was used in calculations. The state of reference is $^1\pi\pi^*$. Negative values are obtained when $S_o$ is stabilized with respect to the $^1\pi\pi^*$ excited state, which translates into a blue-shifted emission.

dipole moments agrees with the small preferential solvation of the ground state over the excited state, and in turn on the small blue-shift observed upon solvation. The theoretical value for the blue-shift of the absorption band maximum in the closed cis enol form is about 1 kcal mol$^{-1}$ in polar solvents, which compares with the experimental value of 2.6 kcal mol$^{-1}$ for HPBI in two independent works[4,7] and of 2.5 kcal mol$^{-1}$ for APBI.[56]

For the keto tautomer, the adiabatic emission energy from the first excited state is 95.2 kcal mol$^{-1}$ and the vertical $^1\pi\pi^* \rightarrow S_o$ emission energy is 88.9 kcal mol$^{-1}$ (the experimental value is 71.5 in ethanol,[5] 60.8[4] kcal mol$^{-1}$ or 59.7[7] kcal mol$^{-1}$ in cyclohexane). With respect to the absorption band corresponding to the closed cis enol form, the largely Stokes-shifted emission of the keto form is computed to be red-shifted by 31.2 kcal mol$^{-1}$ (two experimental values in cyclohexane are available: 24.5[4] and 21.1[7] kcal mol$^{-1}$). Experimentally, this keto emission band maximum is blue-shifted by 5.7 kcal mol$^{-1}$ when going from cyclohexane to water.[4] This result is well reproduced by our MC-FEP results in Table 5, which give a blue-shift of 6.6 kcal mol$^{-1}$ when going from carbon tetrachloride to water. Again, this result can be rationalized from the values of the vertical dipole moments, which are 4.3 and 6.5 D for the $^1\pi\pi^*$ and ground states, respectively. The large stabilization of the ground state as compared to the $^1\pi\pi^*$ excited state, as expected from the dipole moments, agrees with the shift to higher energy as the polarity of the solvent increases. A similar behavior was found in similar species[51,65] and for HPBI in different studies.[4,23]

Finally, as far as the trans enol conformer is concerned, the adiabatic emission energy from the $^1\pi\pi^*$ excited state is 111.0 kcal mol$^{-1}$, while its vertical emission energy is 100.1 kcal mol$^{-1}$. With respect to the absorption band corresponding to the closed cis enol form, the emission of the trans enol form is moderately red-shifted by 10.0 kcal mol$^{-1}$ in the gas phase. Experimentally, this value is only known in methanol (7.5 kcal mol$^{-1}$) and water (6.3 kcal mol$^{-1}$).[4]

## Conclusions

The results presented in this study show that the solvent plays a fundamental role in the relative stabilization of the different ground state rotamers and tautomers of 2-(2′-hydroxyphenyl)-benzimidazole. In the gas phase and for the ground state, the closed cis enol form is the most stable species and is the only form that can exist at significant concentration in apolar or low

polar solvents. Polar and protic solvents, nevertheless, stabilize preferentially the keto and trans enol forms, and this effect is large enough as to bring these species to be in equilibrium with the closed cis enol in aqueous solution. The results show that in water the trans enol conformer, and not the open cis enol as suggested in previous studies, is in equilibrium with the closed cis enol form. These findings suggest that solvation, in conjunction with other factors such as the attachment of particular substituents,[54,58] can be used to control the nature of the processes that occur in the excited states, especially the photoinduced proton transfer.

In the $^1\pi\pi^*$ first excited state and in the gas phase, the keto form is more stable than the closed cis enol and trans enol forms. This justifies the phototautomerization observed from the enol to keto structures in the excited state through the intramolecular proton transfer if the groups involved are suitably arranged, as occurs in the closed cis enol species. The gas phase vertical excitation energy of the closed cis enol form is blue-shifted by 1.0 kcal mol$^{-1}$ in water as compared to the gas phase. The vertical $^1\pi\pi^* \rightarrow S_o$ emission of the keto tautomer is red-shifted with respect to the absorption band of the closed cis enol form, and it is largely blue-shifted as the polarity and hydrogen bonding capacity of the solvent increase. These findings, which are in agreement with available experimental data, show the importance of the environmental effects on the electronic transitions of chemically and biochemically relevant chromophores.

**Acknowledgment.** We are indebted to Prof. J. Tomasi for a copy of his MST code, which was modified by us to perform the present work. We also thank Prof. W. L. Jorgensen for a copy of the BOSS3.4 program. This work has been funded through the Spanish DGICYT Projects No. PB95-0762, PB96-1005 and PB97-0908, and the European Union Project No. CI1*-CT93-0339. The Centre de Supercomputació de Catalunya (CESCA) is acknowledged for financial assistance. One of us (M.F.) thanks the Generalitat de Catalunya for financial help through CIRIT Project No. FI/96-05011.l.

**Supporting Information Available:** Table listing coordinates, total energies, and ESP charges for all optimized stationary points in the ground and the first excited states. This material is available free of charge via the Internet at http://pubs.acs.org.

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