# Computational study of the excited states of 2,5-bis(benzoxazol-2′-yl)-hydroquinone and its monomethoxy derivative

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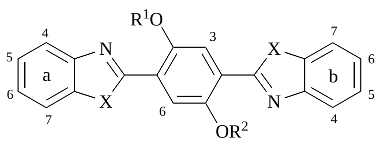
**The geometry of the title compounds in the ground state and in the first excited singlet state have been investigated using AM1 semi-empirical molecular orbital calculations. The data obtained have been employed in a comparative study of the HAM/3 and the INDO/S-CI computational methods for electronic spectra simulation. AM1 results show that the most stable forms of the studied structures are H-bonded structures—enol and keto tautomers for the ground state and first excited singlet state, respectively. Concerning spectroscopic results, INDO/S-CI yields numerical values of excitation energy that better agree with experimental data, while HAM/3 better describes the distribution and relative intensities of the absorption/emission bands.**

Compounds showing excited state intra-molecular proton-transfer reactions (ESIPT) have been declared efficient sources of tuneable stimulated emission[1–3] as well as stabilisers against UV radiation,[4,5] giving rise to renewed interest among photophysicists.[6–19] Their common feature is an unusual very fast proton transfer (Scheme 1), even at low temperatures, from the lowest excited singlet state molecule (${}^1E_1$) to a photo-tautomer (${}^1K_1$).[20,21] After conversion to the ground state (${}^1K_0$), the proton falls back to its original place, regenerating the normal form (${}^1E_0$) without any photochemical change.[18–22] As a result of different absorbing and emitting structures, the emission spectra ($F_k$) of these species show a broad band with a large Stokes shift (6000–10 000 cm$^{-1}$).

$$\begin{tikzcd}
{}^1E_1 \arrow[r] \arrow[d, shift left] & {}^1K_1 \arrow[d] \\
{}^1E_0 \arrow[u, shift left] & {}^1K_0 \arrow[l]
\end{tikzcd}$$

**Scheme 1** Schematic diagram representing ESIPT

In a recent paper,[15] we reported the efficient synthesis and purification of a series of compounds that display ESIPT, the 2,5-bis(benzazol-2′-yl)hydroquinone fluorescent dyes, obtained in the quantity and ultrapure quality needed for laser work. As a rule, no fluorescence ($F_e$) from the enol species (${}^1E_1$) is detected among these aromatic and heteroaromatic molecules, but 2,5-bis(benzoxazol-2′-yl)hydroquinone **1** (BBHQ) and its monomethoxy derivative **2** (BBMP) are exceptions;[21] a dual fluorescence, ascribed to a rapid equilibrium in the excited state,[8,20] is observed for both.



X = O, NH
$R^1 = R^2$ = H, Me, Ac
**1** X = O, $R^1 = R^2$ = H
**2** X = O, $R^1$ = H, $R^2$ = Me

2, 5-Bis(benzazol-2′-yl)hydroquinone dyes

Although the photophysics of BBHQ and BBMP have been extensively investigated,[8–18] some controversies remain. It has been discussed whether the transition occurs with barrierless potential, as part of vibrational redistribution, or proceeds by proton tunnelling through a barrier.[13] A full knowledge of the structure of these compounds in the ground and first excited states, both for the ${}^1E$ and tautomeric ${}^1K$ forms, is very important for the assignment of the emitting species. Semi-empirical and *ab initio* calculations have proved to be a remarkable tool for providing this information; however, only a few theoretical works about ESIPT have been reported.[16–19,23]

In this article, we discuss the preferred conformations of BBHQ and BBMP in the ground and excited states of the enol and tautomeric forms based on semi-empirical molecular orbital calculations with the AM1 hamiltonian. Also, from a comparative study of the results yielded by the spectroscopic methods HAM/3 and INDO/S-CI and the experimental absorption and emission spectra of the title compounds, we draw conclusions about the suitability of the methods for this type of molecule.

## Computational methods

Geometry calculations for tautomers in ground and excited states were carried out using the AM1 method[24] as implemented in the MNDO91 program.[25] Energy was minimised with respect to all geometric variables according to the Davidon–Fletcher–Powell procedure. The AM1 method was chosen due to its special parametrization, which takes hydrogen bonds into account. This is essential for the achievement of reliable data on relative energies between tautomers.

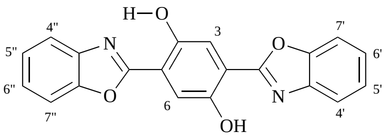
Experimental absorption and emission electronic spectra of BBHQ and BBMP were studied with the semi-empirical methods HAM/3 (hydrogenic atoms in molecule, version 3)[26] and INDO/S-CI (intermediate neglect of differential overlap/spectra-configuration interaction),[27] which have been successfully applied to several molecules. For CI, only one-electron excited configurations were taken into account. In HAM/3, the one-electron two-centre repulsion integrals were evaluated with Mataga's equation. Calculations were carried out on a CRAY Y-MP2E supercomputer.

## Results and discussion

### Molecular geometries

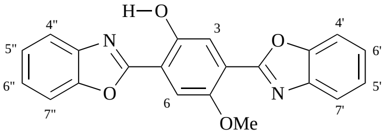
Geometries were fully optimised for BBHQ and BBMP, both in the enol and keto forms, yielding the results summarised in Tables 1 and 2. AM1 calculations rendered a totally planar structure for BBHQ in the ground-state (${}^1E_0$), with strong intramolecular H-bonding, as supported by ${}^1H$ NMR and IR

**Table 1** Results of AM1 calculations for BBHQ

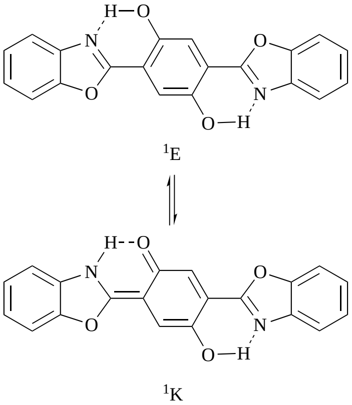


| | | $^1E_0$ | $^1E_1$ | $^1K_0$ | $^1K_1$ |
|---|---|---|---|---|---|
| Bond length/Å | N-3″–H | 2.168 | 2.067 | 0.996 | 1.001 |
| | H–O | 0.969 | 0.980 | 2.178 | 2.100 |
| | O–C-4 | 1.370 | 1.344 | 1.252 | 1.268 |
| | C-4–C-5 | 1.412 | 1.443 | 1.458 | 1.457 |
| | C-5–C-2″ | 1.454 | 1.438 | 1.387 | 1.444 |
| | C-2″–N-3″ | 1.332 | 1.338 | 1.387 | 1.372 |
| Angle/° | N-3″–H–O | 139.5 | 139.9 | 116.4 | 117.5 |
| | H–O–C-4 | 110.2 | 111.5 | 107.3 | 110.0 |
| | O–C-4–C-5 | 126.1 | 124.8 | 123.1 | 121.6 |
| | C-4–C-5–C-2″ | 122.6 | 121.3 | 120.1 | 118.3 |
| | C-5–C-2″–N-3″ | 131.0 | 130.0 | 129.6 | 129.3 |
| | C-2″–N-3″–H | 90.6 | 92.4 | 123.5 | 123.1 |
| Dihedral angle/° | C-4–C-5–C-2″–N-3″ | 0.1 | 0.0 | 0.2 | 0.5 |
| | C-1–C-2–C-2′–N-3′ | 0.2 | 0.1 | 31.4 | 6.7 |

**Table 2** Results of AM1 calculations for BBMP



| | | $^1E_0$ | $^1E_1$ | $^1K_0$ | $^1K_1$ |
|---|---|---|---|---|---|
| Bond length/Å | N-3″–H | 2.171 | 2.057 | 0.996 | 1.002 |
| | H–O | 0.970 | 0.980 | 2.181 | 2.104 |
| | O–C-4 | 1.369 | 1.343 | 1.251 | 1.267 |
| | C-4–C-5 | 1.406 | 1.450 | 1.458 | 1.453 |
| | C-5–C-2″ | 1.453 | 1.435 | 1.385 | 1.447 |
| | C-2″–N-3″ | 1.332 | 1.340 | 1.389 | 1.371 |
| Angle/° | N-3″–H–O | 139.1 | 140.2 | 116.3 | 117.5 |
| | H–O–C-4 | 110.4 | 111.5 | 107.3 | 109.8 |
| | O–C-4–C-5 | 126.2 | 124.6 | 123.1 | 122.0 |
| | C-4–C-5–C-2″ | 122.7 | 121.1 | 120.1 | 118.3 |
| | C-5–C-2″–N-3″ | 130.9 | 130.0 | 129.6 | 129.3 |
| | C-2″–N-3″–H | 90.7 | 92.6 | 123.5 | 123.1 |
| Dihedral angle/° | C-4–C-5–C-2″–N-3″ | 0.3 | 0.0 | 0.0 | 0.7 |
| | C-3–C-2–C-2′–N-3′ | 18.2 | 0.1 | 0.2 | 0.1 |



Enol and keto forms of BBHQ

spectroscopic studies.[20,22] According to AM1, $^1E_1$ is also planar. When compared to MNDO/H calculations,[17] AM1 geometries agree very well, showing only slight differences.

Results for BBHQ in keto form (Table 1) show that the whole structure is changed upon ESIPT. The structure of the central benzene ring changes: the double-bond character of the C-1–C-2, C-3–C-4, C-4–C-5 and C-5–C-6 bonds reduces and that of the C-2–C-3 and C-5–C-6 bonds increases, indicating a slight localisation of double bonds. The highest changes, however, occur for the C-4–O and C-5–C-2″ bonds, which decrease by 0.092 and 0.051 Å, respectively, and for the C-2″–N-3″ bond, which increases by 0.049 Å during the cycle. This would arise from a resonance structure of the keto form that shows some indirect evidence of predominance in the tautomer;[20] nevertheless, a balance between ketonic and zwitterionic structures has been claimed to be closer to reality.[19,28] Finally, the C-1–C-2–C-2′–N-3′ dihedral angle becomes 31.3° larger, whereas the rest of the BBHQ molecule shows only minor changes.

Analogous changes are seen for BBMP (Table 2). Remarkably, the OH→OMe substitution affects planarity (which should be due to hydrogen bond breaking and to steric hindrance provoked by the methoxy group),[16] leading to a decrease in the conjugation of the π system in comparison to BBHQ. The effect is seen as a blue-shift in the absorption and fluorescence spectra.[14]

**Table 3** Excitation energies for BBHQ[a]

| Exper.[b] | | HAM/3 | | | INDO/S-CI | | |
|---|---|---|---|---|---|---|---|
| *E*/eV | log ε | *E*/eV | *f* | CI | *E*/eV | *f* | CI |
| 3.05 | 4.27 | 2.53 | 0.57 | 63→64 | 3.34 | 1.25 | 63→64 |
| 3.17 | 4.26 | 2.86 | 0.34 | 62→64<br>60→64<br>59→65 | | | |
| 3.68 | 4.16 | 3.16 | 0.91 | 62→64<br>60→66 | 3.78 | 0.19 | 61→64<br>63→66 |
| 3.88 | 4.34 | 3.72 | 0.06 | 60→64<br>63→65 | 3.97 | ~ 0 | 62→64<br>63→65 |
| 4.04 | 4.10 | 4.18 | 0.04 | 58→64<br>63→66 | 4.23 | 0.05 | 59→65<br>60→64<br>62→68<br>63→67 |
| | | 4.36 | 0.09 | 61→65<br>63→69 | | | |

[a] $E$ = energy; $f$ = oscillator strength; CI contributions lower than 0.3 are not reported. [b] Ref. 25.

### Assignment of conformers

Our calculations suggest that the most stable ground-state conformer of BBHQ is the one with intramolecular hydrogen bonding between H and N-3″, present in ~77%. This is consistent with the assignment of spectra for BBHQ in solid argon.[13] Conformers in which one or both benzoxazolyl groups are rotated 180° against the hydroquinone centre present higher energies and, hence, appear in lower concentrations. This is in good agreement with experimental estimated data[13,21] and results of MNDO calculations.[17] Although the three species present strong hydrogen bonding, it is believed that the OH···N interaction is stronger[22] than that of OH···O. The open form, present only in strong H-bonding solvents,[8,21] has a negligible contribution in conditions of calculation. It must be kept in mind that AM1 simulates geometries of isolated (gas-phase) molecules.

In the ground state, the calculated energy for the keto species, which exists only as $^1K_1$,[14] is 10.0 kcal mol$^{-1}$ (0.434 eV) above that of the enol structure, in agreement with its absence in the $^1K_0$ state.[13] The barrier to the proton transfer from the $^1K_0$ to the $^1E_0$ state is 20.3 kcal mol$^{-1}$ (0.882 eV). In the excited state, AM1 calculations provide that $^1E_1$ is less stable than $^1K_1$ (8.0 kcal mol$^{-1}$, 0.347 eV), in opposition to MNDO results.[17] The proton transfer barrier in the excited state is slightly lower (15.0 kcal mol$^{-1}$, 0.650 eV) than that calculated for the ground state.

Another important feature of BBHQ is the high HOMO→LUMO contribution to the lowest singlet $^1E_0 \rightarrow {}^1E_1$ transition. The HOMO shows an antibonding character in C-2–C-2′/C-5–C-2″ and is stabilised with ~2.8 kcal mol$^{-1}$ by torsion around these linkages. On the other hand, the LUMO is strongly bonding in these bonds. This contributes to a lack of rotational conformers, tending to stabilise a planar conformation also in the lowest excited singlet state.[16]

Previous studies of structures similar to 2-(2′-hydroxyphenyl)benzoxazole show the interrelation of various ground- and excited-state conformers[22] and discuss the role played by the rotation of the phenyl group. In agreement with what has been reported, calculations with the two ring system out of a plane show poor results. These facts and further evidence[11,13,16] support the assumption that the red fluorescence ($F_k$) observed for BBHQ arises from the excited keto amine structure $^1K$, generated by proton transfer. Along with this species, conformers incapable of undergoing ESIPT (including a hypothetical[13] dimer) appear, yielding the usual[12] blue fluorescence ($F_e$). The largest contributions of $^1E$ and $^1K$ conformers for populations respectively in ground and excited states[17] led us to rationalise spectroscopic calculations, which were performed only on the predominant structures.

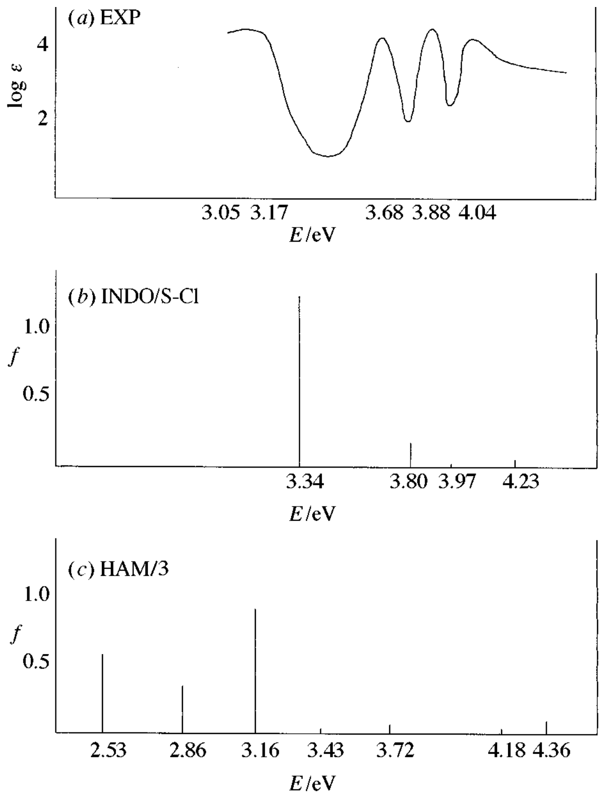


**Fig. 1** Experimental[25] and calculated absorption spectra for BBHQ

### Electronic spectra

**BBHQ.** The results of HAM/3 and INDO/S-CI for excitation energies are listed and compared to experimental data[29] in Table 3. The absorption spectrum shows two bands with maxima at 3.05 and 3.17 eV (Fig. 1). The first observed $^1E_0 \rightarrow {}^1E_1$ transition presents strong HOMO→LUMO character according to both methods. The excited state involved in the second transition was described by HAM/3 mainly with the excited configurations of the valence molecular orbitals 62→64, 60→64 and 59→65, while INDO/S-CI described this state mainly by the 61→64 and 63→66 configurations. This suggests two different transitions, and the lowest electronic transition could be considered of a charge transfer type. The behaviour observed for these transitions in different solvent media[8,21] is in agreement with this assignment. The calculated electronic charge distribution in $^1E_0 \rightarrow {}^1E_1$ shows that the nitrogens in the heterocycles undergo an increase in negative charge density,

**Table 4** Excitation energies for BBMP[a]

| Exper.[b] | | HAM/3 | | | INDO/S-CI | | |
|---|---|---|---|---|---|---|---|
| *E*/eV | log ε | *E*/eV | *f* | CI | *E*/eV | *f* | CI |
| 3.11 (s) | | 2.78 | 0.09 | 66→67 | 2.95 | 0.01 | 62→67<br>62→72 |
| 3.25 | 4.35 | 2.92 | 0.95 | 66→67<br>65→67<br>64→67 | 3.00 | 0.57 | 66→67 |
| 3.72 (s) | | 3.35 | 0.16 | 65→67<br>64→67 | | | |
| 3.83 | 4.47 | 3.50 | 0.17 | 63→67<br>66→68 | 4.17 | 0.28 | 63→67 |

[a] *E* = energy; *f* = oscillator strength; CI contributions lower than 0.3 are not reported. [b] Ref. 25; (s) = shoulder.

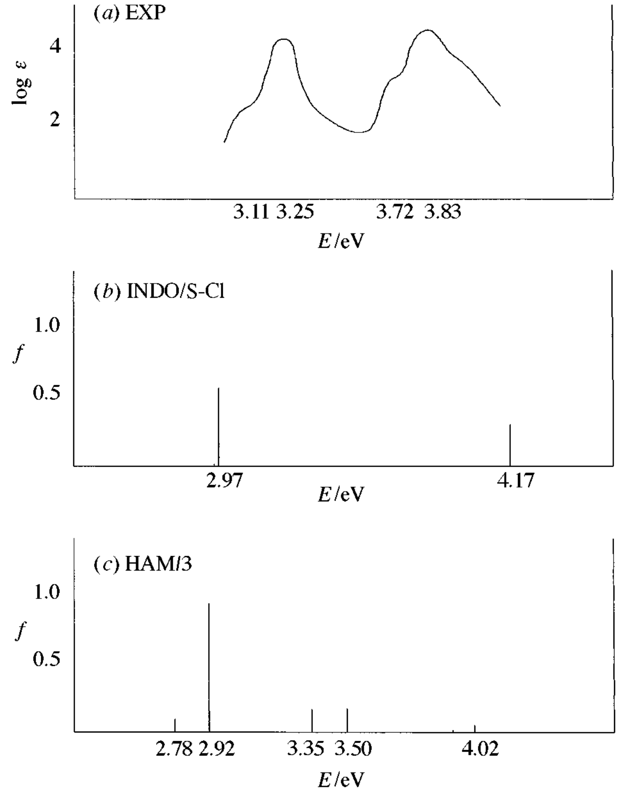


**Fig. 2** Experimental[25] and calculated absorption spectra for BBMP

**Table 5** Emission data for BBHQ

| Fluorescence | Exper.[a] *E*/eV | HAM/3 | INDO/S-CI |
|---|---|---|---|
| $F_e$ | 2.69 | 2.42 | 3.17 |
| $F_k$ | 2.02 | 2.01 | 2.43 |

[a] Ref. 25.

while the phenolic oxygens present an increase in positive charge. Under such conditions, proton transfer is expected to be facilitated,[19] at the same time that strong coupling between electron-donor and electron-acceptor groups in hydrogen bonding systems should reduce internal conversion.[29]

The INDO/S-CI method provided numerical values of excitation energies closer to the experimental ones (Table 3), while HAM/3 rendered a better qualitative description of the observed spectra. Shoulders can be assigned at the HAM/3 level, to an abnormal deviation of average 0.4 eV. This disagreement could be justified by the fact that the method does not take solvent effects into account.

**BBMP.** The calculated values of absorption energies are listed in Table 4. The same qualitative observations valid for the parent compound BBHQ are found. The agreement between observed and calculated transition energies is good for INDO/S, and HAM/3 describes well a band in the absorption spectrum (Fig. 2). A loss of conjugation of the π system by OH→OMe substitution causes a blue-shift in absorption and fluorescence spectra, as mentioned in the previous section. The lowest absorption transition shows strong HOMO→LUMO character according to both calculations, as observed for BBHQ.

**Emission spectra.** The emission process takes place from the excited state equilibrium geometry, which for both BBHQ and BBMP is quite different from that of the ground state, affecting emission spectra. A theoretical value for the Stokes shift observed for the molecules under investigation was obtained through fluorescence calculations on the optimised geometries of the lowest excited states of the enol and keto forms of BBHQ. The lowest transition energy for the excited enol conformer provided by HAM/3 agrees very well with the experimental data for the blue fluorescence (Table 5), and the calculated electronic transition energy for the keto excited form is in good agreement with the measured tautomeric fluorescence. Therefore, our results corroborate previous assignments of emitting species.[11,13,17]

Based on the obtained barrier to proton transfer, a Jablonski diagram can be drawn for BBHQ showing some numerical values (Fig. 3). The data were obtained by different methods of calculation, so that precise comparisons may not be valid; however, order-of-magnitude evaluations can be made. From the ground state, BBHQ shows an absorption of charge transfer type to a single excited state ($^1E_n$). The relaxation process after photoexcitation is a very rapid radiationless decay[14] to the lowest excited singlet state ($^1E_1$). No population is observed[10,13,14] in the triplet state, although HAM/3 yields almost isoenergetic triplet and singlet states (2.44, 2.76, 2.83, 3.02 eV). The low rate of intersystem crossing (ISC) is probably due to a reduced spin-orbit coupling.[4,18] Since hydrogen bonding connects two π systems, a fast mode of non-destructive de-excitation can occur by keto–enol tautomerism followed by a rapid emission ($F_k$) and decay to the $^1K_0$ state. A fast back proton transfer takes place in the ground state and no $^1K_0$ form can be detected, even at low temperatures.[13,21] The $F_e$ emission arises from the transition $^1E_1 \rightarrow {}^1E_0$, which can also occur in competition with ESIPT, but with low[17,20,21] efficiency and intensity. This suggests a low rate for the process. Rates for non-radiative decay (internal conversion) from a lowest excited singlet state in enol and keto forms should be much lower than that of ESIPT and $F_e$ emission.

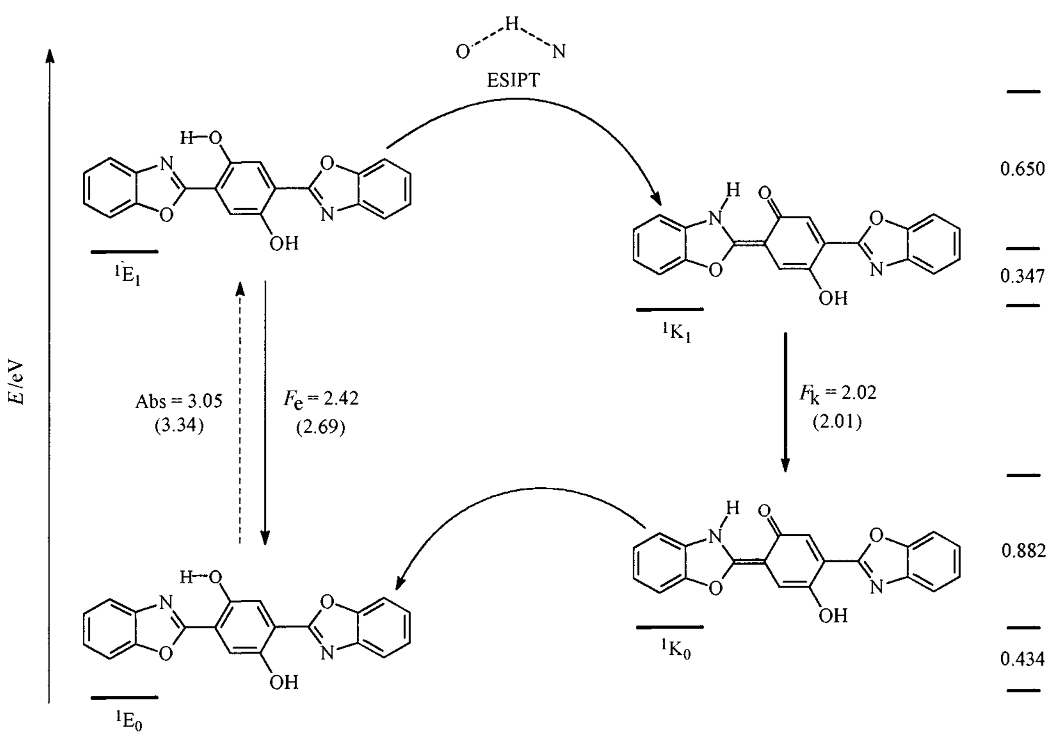


**Fig. 3** Jablonski diagram for BBHQ (experimental values in parentheses)

## Conclusions

The structural and electronic features underlined by semi-empirical AM1 calculations for BBHQ and BBMP agree well with the mechanism currently accepted for ESIPT. The assignment of conformers yielded results similar to those recently obtained by the application of *ab initio* calculations to a similar structure,[23] proving the adequacy of the low cost chosen methods for the proposed work. The spectroscopic results obtained encourage the simultaneous use of HAM/3 and INDO/S-CI methods in the simulation of electronic spectra for the type of molecules studied. Both methods present advantages: HAM/3 in band shape description and INDO/S-CI in the evaluation of numerical energy values. It is expected that improvements in structural computational methods (concerning mainly effects of solute–solvent interaction) are reflected on the performance of future spectroscopic calculations.

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