Heterocyclic dyes displaying excited-state intramolecular proton-transfer reactions (ESIPT): computational study of the substitution effect on the electronic absorption spectra of 2-(2′-hydroxyphenyl)-1,3-benzoxazole derivatives†

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Semi-empirical molecular-orbital methods were used to simulate the electronic absorption spectra of a series of 2-(2′-hydroxyphenyl)-1,3-benzoxazole derivatives, namely AM1 and MNDO-PM3 for geometry optimization and INDO/S-CI and HAM/3 for spectroscopic features. Wavelengths of maximum absorption that agree better with experimental data were found when INDO/S-CI was applied to PM3-generated inputs. Chemical substitution red-shifted the absorption spectrum of all the model compounds, a feature discussed based on the calculated energy levels of frontier orbitals and charge redistribution upon electronic excitation.

Introduction

Chemical compounds displaying excited-state intramolecular proton-transfer reactions (ESIPT) have long been known for their uses as UV-stabilizers,[1] lasing dyes,[2] and, more recently, biological probes,[3,4] as well as their plastic scintillation applications[5] and optical nonlinearities.[6] Much has been established about the mechanisms which underlie their photophysical behaviour,[7] but the tuning of electronic spectra is still a matter of trial and error, often involving laborious and costly laboratory preparations. In a previous paper,[8] we used computational tools to investigate the molecular geometry and spectroscopic properties of 2,5-bis(1,3-benzoxazol-2′-yl)hydroquinone (BBHQ, Fig. 1) and its monomethyl derivative (2,5-bis(1,3-benzoxazol-2′-yl)-4-methoxyphenol, BBMP), chosen as model compounds to study ESIPT, comparing the results to experimental data. We found that structural and electronic features provided by semi-empirical AM1 calculations describe well the mechanism for ESIPT, yielding conformer assignment consistent with expensive high level *ab initio* studies. Spectroscopic calculations using the INDO/S-CI and HAM/3 methods were proved to be valuable for the prediction and interpretation of the visible absorption spectrum of BBHQ and BBMP.

2-(2′-Hydroxyphenyl)-1,3-benzoxazole (HBO, **1**, Fig. 2) is well known to be of importance as the basic skeleton of molecular structures which can undergo ESIPT, including BBHQ, and many experimental studies on its photophysics are available.[9,10] Calculated electronic ground and excited state energies suggest a qualitative four-level diagram (Scheme 1). Bhattacharyya *et al.*[11] have discussed its preferred conformations and assigned a planar conformer as that responsible for absorption. According to them, this should be the result of a conjugative trend towards coplanarity of aromatic rings. In fact, thermal activation at room temperature is of the same order as the calculated energy difference between rotamers, so two significant species should coexist, giving rise to different absorptions and emissions. A broad absorption centered at 318.7 nm has been assigned to the most stable rotamer (form E_0 in Scheme 1).[12] An intense fluorescent emission with maximum yield at 486.2 nm follows, with the large Stokes-shift being explained in terms of an ultra-fast ESIPT process occurring on E_1 which leads to keto–enol tautomerization. The observed

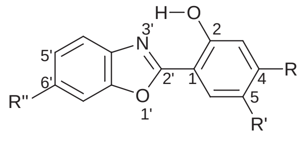
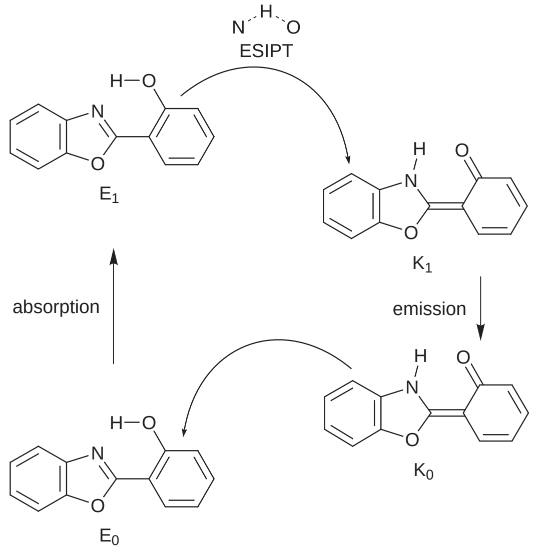


Fig. 2 Benzoxazole structures (see Table 1).



Scheme 1 ESIPT mechanism.

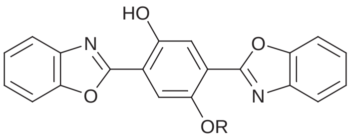


Fig. 1 2,5-Bis(1,3-benzoxazol-2′-yl)hydroquinone dyes (BBHQ, R = H; BBMP, R = Me).

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† Tables containing calculations of optimized geometries, transition energies and oscillator strengths for 13 model compounds are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/1123, otherwise available from BLDSC (SUPPL. NO. 57550, pp. 6) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http:www.rsc.org/authors).

Table 1 Structures investigated

Structure	R	R′	R″
1	H	H	H
2	H	NH_2	H
3	H	NCS	H
4	H	HNCSNH-tBu	H
5	H	H	NH_2
6	COOH	H	NO_2
7	COOH	OH	H
8	COOMe	OH	H
9	COOH	NO_2	NH_2
10	COOH	NO_2	H
11	COOH	NH_2	NO_2
12	COOEt	OH	H
13	COOH	H	NH_2

Table 2 Average of the measures obtained in both geometric methods

		AM1	PM3
Bond Length/Å	N-3′–H	2.166	1.846
	O–H	0.970	0.967
	O–C-2	1.366	1.353
	C-2–C-1	1.410	1.414
	C-1–C-2′	1.452	1.453
	C-2′–N-3′	1.333	1.338
Angle/°	C-2′–N-3′–H	90.78	96.26
	N-3′–H–O	139.05	145.20
	H–O–C-2	110.51	108.98
	O–C-2–C-1	126.16	124.35
	C-2–C-1–C-2′	122.52	119.37
	C-1–C-2′–N-3′	130.92	125.78
Dihedral/°	C-2–C-1–C-2′–N-3′	0.70	0.10

fluorescence is then the result of a transition from K_1 to the unstable K_0 form, which regenerates E_0 once the proton transfer has been reversed. Theoretical studies using *ab initio* and semi-empirical methods have been carried out on this compound, with the emphasis on the relative stabilities of the enol and keto tautomers and their conformers in the S_0 and S_1 states.[13,14]

Spectroscopically parameterized computational methods have made possible a different approach to photophysical investigations. Codes such as INDO/S-CI and HAM/3 have been successfully applied to systematic studies involving a broad range of organic compounds.[15–19] These methods have mainly been used for predicting the maximum wavelengths of absorption and emission using sets of molecular orbital parameters empirically developed for this purpose.[20] Both methods also provide an indication of transition intensity by means of a calculated oscillator strength,[21] and, although less satisfactorily, have been used to calculate other spectroscopic related properties.[15,16,22]

The successful results obtained on BBHQ prompted us to apply semi-empirical methods to examine the effect of chemical substituents on the first excitation energy (wavelength of maximum absorption) of the HBO skeleton from a theoretical standpoint. In this respect, HBO is smaller and should require less time-consuming calculations than BBHQ. A set of sample structures has been conceived, their geometries fully optimized in their fundamental states according to the semi-empirical methods PM3 and AM1, and their visible absorption spectra simulated with INDO/S-CI and HAM/3. The validity of these methods and their combinations is judged on the basis of available experimental data and some conclusions are drawn concerning the effect of the substitution pattern on the wavelength of maximum absorption for the chosen skeleton.

Molecular orbital calculations

The model compounds were investigated in the ground state by using the AM1[23] and MNDO-PM3[24] semi-empirical methods, as implemented on the UniChem 4.1 package.[25] All structures were fully optimised at the Hartree–Fock level on the basis of our previous experience.[8] The S_0 state of the E_0 conformer was assumed to be the most populated, hence it was used as the input for the spectroscopic calculations. Computations were performed at the HAM/3 (Hydrogenic Atoms in Molecule, Version 3)[26] and INDO/S-CI (Intermediate Neglect of Differential Overlap/Spectra-Configuration Interaction, as implemented on the Argus package)[27] levels to evaluate $S_0 - S_1$ transition energies. The 100 configurations of lowest energy were taken into account, namely those obtained by exciting one electron from one of the 10 highest occupied to one of the 10 lowest unoccupied molecular orbitals, using the half-electron approach in the CI treatment. Calculations were carried out on Cray Y-MP2E and T94 supercomputers.

Molecular geometries

Geometries were fully optimised for thirteen molecules (Table 1) as their most stable species (E_0 in Scheme 1). Complete reports are available as supplemental material.† There is in general a good agreement among the results yielded by PM3, AM1, and those reported in previous theoretical studies.[28,29] Nonetheless, PM3 reproduces better the H-bond distances in the site of proton transfer, although it predicts smaller valence angles.

Table 2 shows the average values of the geometry data yielded by PM3 and AM1 calculations for the thirteen model compounds. Even though AM1 values for N-3′–H bond distances and O–C-2–C-1 bond angles (see Fig. 2) are larger than those indicated by PM3, the small discrepancy between data rendered by the different methods should be pointed out. In particular, PM3 computations predict a planar structure for the conformer E_0, in agreement with MNDO.[10,30] Electronic absorption and jet-cooled ^{1}H-NMR spectra support this result.[30] Concerning structures **9** and **13**, AM1 renders a dihedral angle within 1 and 2 degrees between the aromatic rings.

The AM1 method has been extensively tested and proved to be very useful in reproducing several properties among many organic compounds.[31] PM3 still lacks confirmatory evidence of its adequacy in a broad sense. On the other hand, it has supposedly enhanced functions for calculating bond effects at distance.[24] While the AM1 and PM3 methods both use the same semi-empirical implementation of the NDDO approximation they differ in the parametrization procedure. These facts justify the application of both methods to the same set of molecules, since data for direct comparison thus become available. Of relevance to the present work is the fact that apart from small changes in the H-bond site neither of the methods indicates that the introduction of substituents on HBO affects the planar conformation and geometric features of its basic skeleton.

Electronic absorption spectra

The INDO/S-CI and HAM/3 computed $S_1 \leftarrow S_0$ transition energies and oscillator strengths for the absorption spectra of the model compounds are reported in Table 3, together with the corresponding experimental data. The complete set of data is available as supplemental material.† Energy values refer to vertical transitions starting from AM1 and PM3 optimized geometries for the E_0 conformer with an H-bond involving the N atom, in agreement with the assignment of the most populated species in the ground state. Spectroscopic calculations on the HAM/3 level were not performed on structures **3** and **4** due to a lack of parameters for the S atom.

Direct comparison of the results yielded by INDO/S-CI and HAM/3 shows a similar trend for the effect of substituents on the electronic spectra of the structures under investigation. A good linear correlation is observed between the calculated

Table 3 Transition 0–0 and oscillator strength

	Experimental		AM1/INDO		PM3/INDO		AM1/HAM		PM3/HAM	
	E/eV	log ε	*E*/eV	*f*	*E*/eV	*f*	*E*/eV	*f*	*E*/eV	*f*
1	3.75[a]	4.17	3.79	0.71	3.83	0.67	3.36	0.48	3.38	0.36
2	3.37[b]	3.49	3.66	0.54	3.68	0.49	2.86	0.27	2.89	0.27
3	3.56[b]	4.05	3.69	0.58	3.71	0.53	—	—	—	—
4	3.68[b]	4.07	3.72	0.66	3.77	0.61	—	—	—	—
5	—	—	3.57	0.79	3.68	0.76	2.90	0.82	2.99	0.73
6	—	—	3.57	1.03	3.61	0.96	2.77	0.40	2.63	0.37
7	3.21[c]	4.00	3.52	0.69	3.51	0.53	2.79	0.26	2.77	0.28
8	3.23[c]	3.91	3.53	0.69	3.52	0.52	2.78	0.25	2.77	0.29
9	—	—	3.35	0.72	3.55	0.73	2.05	0.60	2.25	0.58
10	—	—	3.68	0.68	3.78	0.64	2.72	0.45	2.86	0.48
11	—	—	3.30	0.51	3.34	0.48	1.86	0.21	1.82	0.19
12	3.19[d]	3.84	3.54	0.68	3.52	0.52	2.80	0.26	2.78	0.29
13	—	—	3.36	0.88	3.54	0.82	2.35	0.84	2.54	0.78

[a] Ref. 12. [b] Ref. 4. [c] Ref. 38. [d] Ref. 39.

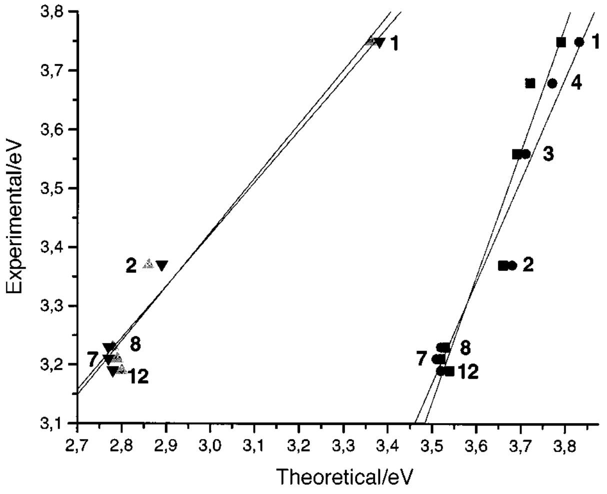

Fig. 3 Maximum absorption against first excitation energies (eV): ■ AM1/INDO, ▲ AM1/HAM, ●; PM3/INDO and ▲ PM3/HAM. (The numbers in the figure refer to the compounds in Table 1).

wavelengths of maximum absorption for HBO and its derivatives and experimental values (Fig. 3). Correlation coefficients for the linear regressions are: for INDO/S-CI, 94 and 96% for calculations using AM1 and PM3-optimised inputs, respectively; for HAM/3, 95 and 98% for data based on the same methods, in the same sequence. This indicates that input geometries generated with PM3 better reproduce experimental excitation energies under both spectroscopic methods. The same behaviour is presented for oscillator strength.

Concerning HAM/3, relative values (*i.e.* compared to HBO) of the transition energies are quite good compared to experimental findings and showed the same trend as those generated by INDO/S-CI. Absolute energies, however, are low compared to both experimental and INDO/S-CI yielded data. The best approximations to experimental data were always given by the combination of PM3 and INDO/S-CI. The excitation energies calculated at the HAM/3 level for the first $\pi^*\leftarrow\pi$ transitions are underestimated by *circa* 0.5 eV. Underestimation of these energies is a characteristic not only of HAM/3, but also of CNDO.[32] This observation can be explained in terms of the Franck–Condon principle. It is known that electronic excitation induces geometry changes on the absorbant species—here, E_0. According to our calculations, the C-2–O and C-1–C-2′ bond lengths are specially affected, suggesting a slight localization of double bonds.[8] Vertical excitation energies are then greater than the 0–0 transition energy.

The electronic state associated with each transition can be quantitatively evaluated through the oscillator strength, which reflects the typical relationship between molar absorption coefficients and allowed, partially allowed, or forbidden transitions.[21] According to our calculations, the electronic transitions under consideration are of the $\pi^*\leftarrow\pi$ type. It is known that the presence of H-bonds in solution destabilises the n,π* states and stabilises the π,π* ones, leading in some cases to energy inversion. Our calculations show such an inversion for HBO and its derivatives, which should be due to intramolecular interaction between the H-atom and the free electron pair of N-3′. Therefore, $\pi^*\leftarrow n$ transitions are shifted to higher frequencies. Similar systems have shown the same behaviour.[33] The wavelength of maximum absorption is always predicted to originate from a singlet–singlet transition. Even though HAM/3 yields nearly degenerate triplet states, a low yield of intersystem crossing (ISC) is expected due to reduced spin–orbit coupling.[1a,34]

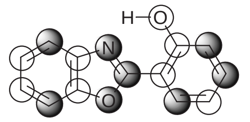

Fig. 4 π-Electronic density changes in HBO and derivatives using INDO/PM3 calculations for the electronic S_0–S_1 transitions (grey circles = increase; open circles = decrease).

Calculated data show that all $S_1\leftarrow S_0$ transitions are closely related to the HOMO–LUMO orbitals, and both INDO/S-CI and HAM/3 indicate charge-transfer from aromatic rings to the oxazole ring (Fig. 4). This is also supported by the variation of dipole momentum observed as a consequence of these transitions. The effect of substituents on color depends largely on the electron-donor/electron-acceptor power of the substituents. There is a red-shift in the first absorption band of all derivatives compared to that of HBO, probably caused by destabilization of the HOMO orbital due to the greater electronic density.

Table 3 shows small changes in the theoretical description of singlet electronic absorption spectra on going from HBO to its derivatives; more specifically, there is a slight variation of energy and oscillator strength for $\pi^*\leftarrow\pi$ transitions. As a general trend, all substituents lead to a red-shift, but replacement of H at the R, R′, or R″ position (see Fig. 2) does result in distinct bathochromic shifts for the wavelengths of maximum absorption. Again the effect of chemical substitution depends on the electron-donor/acceptor power of the substituents. The red-shifts calculated for HBO derivatives as compared to the parent compound can be interpreted in terms of the energy levels of the frontier orbitals as an indication of HOMO destabilization.

According to our calculations, the wavelength of maximum absorption undergoes greater shifts when an electron-withdrawing group is placed at position R″ (**6** *versus* **10**), and this effect increases when position R′ is occupied by an electron-donor moiety (**7** *versus* **10**). It has been reported that modification of 2-(2′-hydroxyphenyl)benzimidazole (HPB)[35] by the introduction of an electron-withdrawing substituent at the position corresponding to R′ considerably shifts its wavelength of maximum absorption to the red end of the visible spectrum.[2d]

Electron-withdrawing groups such as ethoxycarbonyl and nitro placed at R and R″ (**11**) seem to be more effective in promoting the red-shift, although at the expense of a reduction in oscillator strength. The electron-donor groups amino, isothiocyanate, and *N-tert*-butylthioureide (**2**, **3** and **4**) placed at position R′ have little effect on the absorption maximum of HBO. The existence of such an effect should be due to an internal electronic resonance.

The good agreement between experimental and calculated data (Fig. 3) proves the usefulness of the employed theoretical methods in predicting the optical properties of the class of compounds under investigation. One could expect that the energy effect of a double substitution should be roughly the sum of the effects of the two single substitutions, however there is a synergistic effect, probably due to the two aromatic rings being connected to each other, not acting as an isolated system. Also to a lesser extent it is due to the intramolecular H-bonding interaction which stabilises the system.[36,37] Unsynthesized structure **11**, for instance, is expected to red-shift the simulated absorption maximum of HBO (3.83 eV according to PM3-INDO) by 0.49 eV (to 3.34 eV according to the same methods). The effect can be attributed to electronic delocalization promoted by the electron-donor moiety amino at position R′ added to the effect of the nitro group at R″. This assumption is supported by the absorption values found for molecules **2** and **6**.

Electronic densities

The results calculated for all the studied compounds can be explained on the basis of electron donation and withdrawal. INDO/S-CI simulations also provide some insight into the electronic rearrangement which follows a ${}^1S_1 \leftarrow {}^1S_0$ transition. This is illustrated for HBO in Fig. 4. The π-electron density on the 6-membered ring of the benzoxazole moiety decreases. In their turn, O-2, C-2′, and N-3′ gain electronic density upon molecular excitation, while C-1, C-2, and O-1′ have the opposite effect—characterizing a typical donor–acceptor chromogen. Proton transfer is expected to be strongly favored in the first excited state, since data indicate an increase of the π-electron density on N-3′ and a reduction on O-1′. Indeed, differences in acidity and basicity are expected upon excitation.[36] Derivatives **9** and **13** showed the largest positive electron load variations on N-3′, but without a corresponding reduction of electronic density over O-2. As judged by the spectroscopic results observed for the whole set of simulated structures, this suggests a special role for N-3′ in the red-shift of absorption maxima. The acid–base reasoning also explains the greatest red-shift calculated for structures presenting an electron-donor at R′ and an electron-acceptor at R″.

Conclusion

Semi-empirical methods, namely MNDO-PM3 and AM1 (for geometry optimization) and INDO/S-CI and HAM/3 (for spectroscopic analysis), were applied to simulate the structural and electronic features of a series of HBO derivatives. The calculated quantities were compared among themselves and with experimental data. From the results obtained, one notices that: (i) spectroscopic calculations depend on the input geometry, PM3 being superior to AM1 for structural simulation; (ii) compared to HAM/3, INDO/S-CI gives values for the energies of maximum absorption which better reproduce experimental data and (iii) the effect of substituents on the calculated electronic absorption spectra of the structures under investigation is well rationalized with its basis in electron-donor and electron-acceptor characteristics and electronic loading promoted by optical excitation.

Although uncertainties arise from the neglect of solvent effects and many approximations have been made in both spectroscopic methods, the results obtained are in good agreement with experimental data. Our findings support all the available data concerning HBO and its derivatives and can possibly be extended to a wider range of compounds displaying ESIPT. It seems to be clear that suitable substitution can open a wide field of research for HBO derivatives and related compounds, and that INDO/S-CI will allow new approaches on the theoretical building of new materials for a broad range of applications. This highlights the complementarity between theory and experiment for the solution of complex problems. With theoretical guidance, one can select a few candidates for actual synthesis, saving the time and money which would be used in doubtful synthetic work. At the moment, our group is investigating synthetic routes to derivatives **5** and **9**, as well as simulating the photophysical behaviour of a series of benzimidazoles.

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