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—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 as well as stabilisers against UV radiation, giving rise to renewed interest among photophysicists. Their common feature is an unusual very fast proton transfer (Scheme 1), even at low temperatures, from the lowest excited singlet state molecule (\(^1E_0\)) to a phototautomer (\(^1K_0\)). 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. As a result of different absorbing and emitting structures, the emission spectra (\(F_\lambda\)) of these species show a broad band with a large Stokes shift (6000–10 000 cm\(^{-1}\)).

In a recent paper, the efficient synthesis and purification of a series of compounds that display ESIPT, the 2,5-bis(benzoxazol-2'-yl)hydroquinone fluorescent dyes, obtained in the quantity and ultrapure quality needed for laser work. As a rule, no fluorescence (\(F_\lambda\)) from the enol species (\(^1E_0\)) 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; a dual fluorescence, ascribed to a rapid equilibrium in the excited state, is observed for both. Although the photophysics of BBHQ and BBMP have been extensively investigated, 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. 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.

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.

**C computational methods**

Geometry calculations for tautomers in ground and excited states were carried out using the AM1 method as implemented in the MNDO91 program. Energy was minimised with respect to all geometric variables according to the Daidon-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) and INDO/S-CI (intermediate neglect of differential overlap/spectra-configuration interaction), 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 M ataga’s equation. Calculations were carried out on a CRAY Y-M P2E 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

<table>
<thead>
<tr>
<th>Bond length/Å</th>
<th>N-3'-H</th>
<th>O-3'–H</th>
<th>C-2–N-3</th>
<th>C-2–C-3</th>
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<tr>
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<td>2.067</td>
<td>0.996</td>
<td>1.001</td>
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<td>O-3'–H</td>
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<td>0.980</td>
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<td>2.100</td>
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<td>C-2–N-3</td>
<td>1.370</td>
<td>1.344</td>
<td>1.252</td>
<td>1.268</td>
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<td>C-2–C-3</td>
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<td>C-2–C-4</td>
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</table>

<table>
<thead>
<tr>
<th>Angle/°</th>
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<th>O-3'–H–O</th>
<th>C-2–C-3</th>
<th>C-2–C-4</th>
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<tr>
<td>N-3'–H–O</td>
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<td>139.9</td>
<td>116.4</td>
<td>117.5</td>
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<tr>
<td>O-3'–H–O</td>
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<td>C-2–C-3–C-4</td>
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<td>123.1</td>
<td>121.6</td>
</tr>
<tr>
<td>C-2–C-4–C-5</td>
<td>122.6</td>
<td>121.3</td>
<td>120.1</td>
<td>118.3</td>
</tr>
<tr>
<td>C-2–C-4–C-5</td>
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</table>

<table>
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<tr>
<th>Dihedral angle/°</th>
<th>C-2–C-4–C-5</th>
<th>C-2–C-4–C-5</th>
<th>C-2–C-4–C-5</th>
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<tr>
<td>N-3'–H–O–C-2</td>
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<td>123.1</td>
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</table>

Table 2  Results of AM1 calculations for BBMP

<table>
<thead>
<tr>
<th>Bond length/Å</th>
<th>N-3'-H</th>
<th>O-3'–H</th>
<th>C-2–N-3'</th>
<th>C-2–C-3'</th>
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</thead>
<tbody>
<tr>
<td>N-3'–H</td>
<td>2.171</td>
<td>2.057</td>
<td>0.996</td>
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<tr>
<td>O-3'–H</td>
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<td>0.980</td>
<td>2.181</td>
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<td>C-2–N-3'</td>
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<td>1.267</td>
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<tr>
<td>C-2–C-3'</td>
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<td>C-2–C-4’-N-3</td>
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<td>C-2–C-4’-N-3</td>
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<td>1.340</td>
<td>1.389</td>
<td>1.371</td>
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<table>
<thead>
<tr>
<th>Angle/°</th>
<th>N-3'–H–O</th>
<th>O-3'–H–O</th>
<th>C-2–C-3</th>
<th>C-2–C-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-3'–H–O</td>
<td>139.1</td>
<td>140.2</td>
<td>116.3</td>
<td>117.5</td>
</tr>
<tr>
<td>O-3'–H–O</td>
<td>110.4</td>
<td>111.5</td>
<td>107.3</td>
<td>109.8</td>
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<tr>
<td>C-2–C-3–C-4</td>
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<td>124.6</td>
<td>123.1</td>
<td>122.0</td>
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<tr>
<td>C-2–C-4–C-5</td>
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<td>121.1</td>
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<tr>
<td>C-2–C-4–C-5</td>
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<tr>
<td>C-2–C-4–C-5</td>
<td>90.7</td>
<td>92.6</td>
<td>123.5</td>
<td>123.1</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Dihedral angle/°</th>
<th>C-2–C-4–C-5</th>
<th>C-2–C-4–C-5</th>
<th>C-2–C-4–C-5</th>
<th>C-2–C-4–C-5</th>
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<tbody>
<tr>
<td>N-3'–H–O–C-2</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.7</td>
</tr>
<tr>
<td>C-2–C-4–C-5–N-3'</td>
<td>18.2</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
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</tbody>
</table>

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 tautomeric form. Nevertheless, a balance between ketonic and zwitterionic structures has been claimed to be closer to reality. 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), 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.

spectroscopic studies. According to AM1, the enol form is also planar. When compared to MNDO/H calculations, 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 tautomeric form. Nevertheless, a balance between ketonic and zwitterionic structures has been claimed to be closer to reality. 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.

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for BBHQ arises from the excited keto amine structure.

Results of MNDO calculations. Along with this species, con-

formers, tending to stabilise a planar conformation also in

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

support the assumption that the red fluorescence \((F_{\text{red}})\) observed for BBHQ arises from the excited keto amine structure \(K^*\), generated by proton transfer. Along with this species, con-

formers incapable of undergoing ESPT (including a hypo-

thetical \(K^*\) dimer) appear, yielding the usual\(^{12}\) blue fluorescence \(F_{\text{blue}}\). The largest contributions of \(K^*\) and \(K\) formers for populations respectively in ground and excited states\(^{25}\) led us to rationalise spectroscopic calculations, which were performed only on the predominant structures.

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 consist-

ent with the assignment of spectra for BBHQ in solid argon.\(^{13}\)

Conformers in which one or both benzoazoxyl 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 \(\text{M N D O}\) calculations.\(^{13}\) Although the three species

present strong hydrogen bonding, it is believed that the

OH \( \cdots \cdot N\) interaction is stronger\(^{23}\) than that of OH \( \cdots \cdot O\). The

open form, present only in strong H-bonding solvents,\(^{13,23}\) has a

negligible contribution in conditions of calculation. It must

be kept in mind that \(\text{A M 1}\) simulates geometries of isolated

(gas-phase) molecules.

In the ground state, the calculated energy for the keto species,

which exists only as \(K\),\(^{14}\) is 10.0 kcal mol\(^{-1}\) (0.434 eV) above

that of the enol structure, in agreement with its absence in the

\(K^*\) state.\(^{13}\) The barrier to the proton transfer from the \(K\) to

to the \(E^*\) state is 20.3 kcal mol\(^{-1}\) (0.882 eV). In the excited state,

\(\text{A M 1}\) calculations provide that \(E^*\) is less stable than \(K\) (8.0

cal/mol, 0.347 eV), in opposition to \(\text{M N D O}\) results.\(^{17}\) The

proton transfer barrier in the excited state is slightly lower (15.0

cal/mol, 0.650 eV) than that calculated for the ground state.

Another important feature of BBHQ is the high HOMO \(\rightarrow\)

LUMO contribution to the lowest singlet \(E_{\text{S}-\text{E}_1}\) transition. The

HOMO shows an antibonding character in C-2-C-2'/

C-5-C-5' and is stabilised with \(\approx 2.8\) 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.\(^{26}\)

Previous studies of structures similar to 2-(2-hydroxy-

phenyl)benzoxazole show the interrelation of various ground-

and excited-state conformers\(^{22,26}\) 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\(^{11,13,25}\)

support the assumption that the red fluorescence \(F_{\text{red}}\) observed for BBHQ arises from the excited keto amine structure \(K^*\),
generated by proton transfer. Along with this species, con-

formers incapable of undergoing ESPT (including a hypo-

thetical \(K^*\) dimer) appear, yielding the usual\(^{12}\) blue fluorescence

\(F_{\text{blue}}\). The largest contributions of \(E^*\) and \(K\) formers for

populations respectively in ground and excited states\(^{25}\) led us to

rationalise spectroscopic calculations, which were performed

only on the predominant structures.

Table 3

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Excitation energies for BBHQ *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp, b</td>
</tr>
<tr>
<td>E / eV</td>
<td>f / CI</td>
</tr>
<tr>
<td>3.05</td>
<td>4.27</td>
</tr>
<tr>
<td>3.17</td>
<td>4.26</td>
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<tr>
<td>3.68</td>
<td>4.16</td>
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<td>3.88</td>
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<td></td>
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</tr>
</tbody>
</table>

* E = energy; f = oscillator strength; CI contributions lower than 0.3 are not reported. *Ref. 25.

Electronic spectra

BBHQ. The results of \(\text{H A M / 3}\) and \(\text{I N D O / S - C I}\) for exci-
tation energies are listed and compared to experimental data\(^{25}\)
in Table 3. The absorption spectrum shows two bands with

maxima at 3.05 and 3.17 eV (Fig. 1). The first observed \(E_{\text{S}-\text{E}_1}\)

transition presents strong HOMO \(\rightarrow\) LUMO character accord-
ing to both methods. The excited state involved in the second

transition was described by \(\text{H A M / 3}\) mainly with the excited

configurations of the valence molecular orbitals 62→64, 60→64

and 59→65, while \(\text{I N D O / S - C I}\) 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\(^{29}\) is in

agreement with this assignment. The calculated electronic

charge distribution in \(E_{\text{S}-\text{E}_1}\) shows that the nitrogens in the

heterocycles undergo an increase in negative charge density.
ing systems should reduce internal conversion.

electron-donor and electron-acceptor groups in hydrogen bond-


not take solvent effects into account. Agreement could be justified by the fact that the method does
level, to an abnormal deviation of average 0.4 eV. This dis-

observed spectra. Shoulders can be assigned at the HAM/3
tation energies closer to the experimental ones (Table 3), while

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

The INDO/S-CI method provided numerical values of exci-
tation 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 dis-

agreement 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

while the phenolic oxygens present an increase in positive
core 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 fluores-
cence. Therefore, our results corroborate previous assignments
of emitting species.

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; how-
ever, order-of-magnitude evaluations can be made. From the
ground state, BBHQ shows an absorption of charge transfer
character according to both calculations, as observed for
BBHQ.

**BBMP**.

Table 4 Excitation energies for BBMP

<table>
<thead>
<tr>
<th>E/ex</th>
<th>loge</th>
<th>Ham/3</th>
<th>INDOS-CI</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>E/eV</td>
<td>f</td>
</tr>
<tr>
<td>3.11</td>
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<td>66→67</td>
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<tr>
<td>3.25</td>
<td>4.35</td>
<td>2.92</td>
<td>66→67</td>
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<td>3.72</td>
<td>3.35</td>
<td>0.16</td>
<td>65→67</td>
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<tr>
<td>3.83</td>
<td>4.47</td>
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<td>63→67</td>
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</table>

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

Table 5 Emission data for BBHQ

<table>
<thead>
<tr>
<th></th>
<th>Exper.</th>
<th>E/ex</th>
<th>Ham/3</th>
<th>INDOS-CI</th>
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<td>F_k</td>
<td>2.69</td>
<td>2.42</td>
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<tr>
<td>F_e</td>
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<td>2.01</td>
<td>2.43</td>
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</table>

* Ref. 25.
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, 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.

Acknowledgements

The authors are grateful for financial support from The Conselho Nacional para o Desenvolvimento Científico e Tecnológico (CNPq) and The Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS). Computational facilities were made available by The Centro Nacional de Supercomputação (CESUP/UFRGS). Professor J. Schifino’s proof-reading is greatly acknowledged.

References