SPATIAL CONFIGURATION
OF DERIVATIVES OF
5,5a,6,7-TETRAHYDROPYRIDO-
[1,2-a]BENZIMIDAZOLE AND
6,7-DIHYDRO-5aH-PYRIDO-
[1,2-b]BENZOXAZOLE

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The spatial configurations of 7,9-diphenyl-5a,6-tetramethylene-5,5a,6,7-tetrahydropyrido[1,2-a]-
benzimidazole and 7,9-diphenyl-5a,6-tetramethylene-2,5a,6,7-tetrahydropyrido[1,2-a]benzimidazol-2-one
have been established by X-ray crystallography. Analogous configurations are proposed for a series of other derivatives of 5,5a,6,7-tetrahydropyrido[1,2-a]benzimidazoles and some derivatives of
6,7-dihydro-5aH-pyrido[1,2-b]benzoxazoles on the basis of ¹H NMR spectroscopic data and the results
of quantum chemical calculations using the MNDO, AM1, and PM3 methods.

Keywords: pyrido[1,2-a]benzimidazoles, pyrido[1,2-b]benzoxazoles, X-ray crystallographic analysis,
quantum-chemical calculations.

Derivatives of 5,5a,6,7-tetrahydropyrido[1,2-a]benzimidazole (1, 3, 5, 7, 9) and 6,7-dihydro-5aH-
pyrido[1,2-b]benzoxazole (2, 4, 6, 8) are formed by the reaction of 1,5-diketones with o-phenylenediamine and
o-aminophenol respectively [1, 2].

Derivatives of 5,5a,6,7-tetrahydropyrido[1,2-a]benzimidazol-2-one (10-14) were obtained by oxidation
of the corresponding 5,5a,6,7-tetrahydropyrido[1,2-a]benzimidazoles [3]. In the ¹H NMR spectra of all of these
compounds, except the 5,5a,6,7-tetrahydropyrido[1,2-a]benzimidazoles 9 and 14, a shift of the signal of one of
the aromatic protons (a quinoid proton in compounds 10-13) to high field was observed (Table 1). This signal is
assigned to proton 1-H, which is close to the aromatic ring bonded to position 9. From an examination of models
taking into account this assignment cis coupling of the tetrahydropyridine (A) and azoline (B) rings with a
pseudoaxial position of the N₁₇₋C₁₀₅ bond relative to ring A is proposed. This in turn assumes cis coupling
of the tetrahydropyridine and the alicyclic side chain units (e.g., A/D coupling in compounds 3 and 11). These
same proposals were suggested previously for the configuration of the products of the reactions of o-carboxyl
substituted hemicyclic 1,5-diketones with o-aminophenol and o-phenylenediamine [4].

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TABLE 1. Chemical Shifts (δ, ppm) for the H$_{1}$ Protons in Compounds 1-14

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ</th>
<th>Compound</th>
<th>δ</th>
<th>Compound</th>
<th>δ$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>5.81</td>
<td>4b</td>
<td>5.75</td>
<td>10a</td>
<td>4.85</td>
</tr>
<tr>
<td>1b</td>
<td>5.91</td>
<td>5</td>
<td>6.09</td>
<td>10b</td>
<td>4.94</td>
</tr>
<tr>
<td>2</td>
<td>5.81</td>
<td>6a</td>
<td>6.11</td>
<td>11</td>
<td>4.76</td>
</tr>
<tr>
<td>3a</td>
<td>5.65</td>
<td>6b</td>
<td>6.19</td>
<td>12</td>
<td>5.25</td>
</tr>
<tr>
<td>3b</td>
<td>5.70</td>
<td>7</td>
<td>6.15</td>
<td>13</td>
<td>5.30</td>
</tr>
<tr>
<td>3c</td>
<td>5.63</td>
<td>8</td>
<td>6.30</td>
<td>14a</td>
<td>5.74</td>
</tr>
<tr>
<td>3d</td>
<td>5.34</td>
<td>9a</td>
<td>6.60</td>
<td>14b</td>
<td>5.83</td>
</tr>
<tr>
<td>4a</td>
<td>5.71</td>
<td>9b</td>
<td>6.65</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Doublet with $J_{1,2}$ of the order of 7 Hz.

*² Doublet with $J_{1,3}$ of the order of 2 Hz.