Selective Recognition of Neurotransmitters in Aqueous Solution by Hydroxyphenyl Aza-Scorpiand Ligands.

Begoña Verdejo, Mario Inclán, Salvador Blasco, Rafael Ballesteros-Garrido, Matteo Savastano, Antonio Bianchi, and Enrique García-España.
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**Figure S1.** Distribution diagram for L2 overlapped to UV-VIS data for 293 nm. Determined in 0.15 mol·dm\(^{-3}\) NaCl at 298.1 ± 0.1 K with [L1] = 10\(^{-4}\) mol·dm\(^{-3}\)

**Figure S2.** Distribution diagram for L3 overlapped to UV-VIS data for 293 nm. Determined in 0.15 mol·dm\(^{-3}\) NaCl at 298.1 ± 0.1 K with [L1] = 10\(^{-4}\) mol·dm\(^{-3}\)

**Figure S3.** Variation of the \(^1\)H NMR spectra of L1 with pD.

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**Table S5.** Thermodynamic data for ligands and neurotransmitters protonation and for formation of L1 complexes with serotonin determined at 298.1 K in 0.15 mol·dm\(^{-3}\) NaCl.
**Figure S1.** Distribution diagram for L2 overlapped to UV-VIS data for 293 nm.

Determined in 0.15 mol·dm\(^{-3}\) NaCl at 298.1 ± 0.1 K with \([L2] = 10^{-4}\) mol·dm\(^{-3}\)
**Figure S2.** Distribution diagram for L3 overlapped to UV-VIS data for 293 nm.

Determined in 0.15 mol·dm$^{-3}$ NaCl at 298.1 $\pm$ 0.1 K with $[L3] = 10^{-4}$ mol·dm$^{-3}$
Figure S3. Variation of the $^1$H NMR spectra of L1 with pD.
Figure S4. Variation of the $^{13}$C NMR spectra of L1 with pD.
Table S1. Stepwise protonation constants for L3 determined at 298.1 K in 0.15 mol·dm$^{-3}$ NaCl

The analysis of different UV–Vis data sets centered on the phenolate band by HypSpec program,i allows to calculate a pK value of de 9.53 (2), 8.40 (3) y 7.20 (4) for L3. These values are in agreement with the results obtained by the potentiometric measurements.

<table>
<thead>
<tr>
<th>Reaction$^a$</th>
<th>UV-Visible</th>
<th>EMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>H+$^+$ L ⇋ HL</td>
<td>-</td>
<td>10.153(9)</td>
</tr>
<tr>
<td>H + HL ⇋ H$_2$L</td>
<td>9.53 (2)</td>
<td>9.473(9)</td>
</tr>
<tr>
<td>H + H$_2$L ⇋ H$_3$L</td>
<td>8.40 (3)</td>
<td>8.516(8)</td>
</tr>
<tr>
<td>H + H$_3$L ⇋ H$_4$L</td>
<td>7.20 (4)</td>
<td>7.341(9)</td>
</tr>
</tbody>
</table>

(a) Charges omitted. (b) Values in parenthesis are standard deviations in the last significant figure.
**Table S2.** Stepwise stability constants for the formation of dopamine complexes with L1 – L4 in 0.15 mol·dm$^{-3}$ NaCl at 298.1 K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>L1</th>
<th>L2</th>
<th>L3</th>
<th>L4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AH} + \text{L} \rightleftharpoons \text{AHL}^a$</td>
<td>–</td>
<td>–</td>
<td>3.39 (6)</td>
<td>–</td>
</tr>
<tr>
<td>$\text{HA} + \text{HL} \rightleftharpoons \text{AH}_2\text{L}$</td>
<td>3.37 (8) $^b$</td>
<td>3.63 (6)</td>
<td>4.07 (4)</td>
<td>3.25 (5)</td>
</tr>
<tr>
<td>$\text{H}_2\text{A} + \text{L} \rightleftharpoons \text{AH}_2\text{L}$</td>
<td>–</td>
<td>–</td>
<td>3.82 (4)</td>
<td>–</td>
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<tr>
<td>$\text{H}_2\text{A} + \text{HL} \rightleftharpoons \text{AH}_3\text{L}$</td>
<td>3.76 (2)</td>
<td>3.54 (3)</td>
<td>3.77 (4)</td>
<td>3.03 (3)</td>
</tr>
<tr>
<td>$\text{H}_2\text{A} + \text{H}_2\text{L} \rightleftharpoons \text{AH}_4\text{L}$</td>
<td>4.13 (3)</td>
<td>3.60 (6)</td>
<td>4.18 (4)</td>
<td>3.44 (4)</td>
</tr>
<tr>
<td>$\text{H}_3\text{A} + \text{HL} \rightleftharpoons \text{AH}_4\text{L}$</td>
<td>–</td>
<td>–</td>
<td>4.10 (4)</td>
<td>–</td>
</tr>
<tr>
<td>$\text{H}_3\text{A} + \text{H}_2\text{L} \rightleftharpoons \text{AH}_5\text{L}$</td>
<td>3.98 (3)</td>
<td>3.78 (4)</td>
<td>3.87 (4)</td>
<td>3.32 (3)</td>
</tr>
<tr>
<td>$\text{H}_3\text{A} + \text{H}_3\text{L} \rightleftharpoons \text{AH}_6\text{L}$</td>
<td>4.01 (3)</td>
<td>3.62 (4)</td>
<td>3.85 (4)</td>
<td>3.33 (3)</td>
</tr>
<tr>
<td>$\text{H}_3\text{A} + \text{H}_4\text{L} \rightleftharpoons \text{AH}_7\text{L}$</td>
<td>3.95 (7)</td>
<td>3.51 (5)</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

(a) Charges omitted. b) Values in parenthesis are standard deviations in the last significant figure.
Table S3. Stepwise stability constants for the formation of serotonin complexes with L1 – L5 in 0.15 mol·dm⁻³ NaCl at 298.1 K

- Charges omitted. b) Values in parenthesis are standard deviations in the last significant figure.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>L1</th>
<th>L2</th>
<th>L3</th>
<th>L4</th>
<th>L5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL + HA ⇌ H₂LA</td>
<td>4.14 (2) b</td>
<td>3.22(3)</td>
<td>3.74 (2)</td>
<td>2.97(3)</td>
<td>2.89(2)</td>
</tr>
<tr>
<td>HL + H₂A ⇌ H₃LA</td>
<td>4.23 (1)</td>
<td>3.00(3)</td>
<td>3.57 (2)</td>
<td>2.73(2)</td>
<td>2.87(2)</td>
</tr>
<tr>
<td>H₂L + H₂A ⇌ H₄LA</td>
<td>4.60 (1)</td>
<td>2.72(4)</td>
<td>3.61 (2)</td>
<td>2.95(2)</td>
<td>2.77(1)</td>
</tr>
<tr>
<td>H₃L + H₂A ⇌ H₅LA</td>
<td>4.93 (2)</td>
<td>2.32(7)</td>
<td>3.53 (3)</td>
<td>3.21(2)</td>
<td>2.76(1)</td>
</tr>
<tr>
<td>H₄L + H₂A ⇌ H₆LA</td>
<td>5.11 (3)</td>
<td>3.48 (2)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
**Table S4.** Stepwise stability constants for the formation of tyramine complexes with \( \textbf{L1} \) – \( \textbf{L5} \) in 0.15 mol·dm\(^{-3}\) NaCl at 298.1 K

\[ \Delta \] in 0.15 mol·dm\(^{-3}\) NaCl at 298.1 K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>L1</th>
<th>L2</th>
<th>L3</th>
<th>L4</th>
<th>L5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL + A ⇌ HLA</td>
<td>–</td>
<td>–</td>
<td>2.93(8)</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>HL + HA ⇌ H(_2)LA (^a)</td>
<td>3.13(3) (^b)</td>
<td>3.68(2)</td>
<td>3.31(2)</td>
<td>3.18(3)</td>
<td>–</td>
</tr>
<tr>
<td>H(_2)L + HA ⇌ H(_3)LA</td>
<td>-</td>
<td>3.73(2)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>HL + H(_2)A ⇌ H(_3)LA</td>
<td>3.67(2)</td>
<td>-</td>
<td>3.61(2)</td>
<td>3.35(4)</td>
<td>–</td>
</tr>
<tr>
<td>H(_2)L + H(_2)A ⇌ H(_4)LA</td>
<td>3.49(2)</td>
<td>3.83(2)</td>
<td>3.54(2)</td>
<td>3.35(3)</td>
<td>–</td>
</tr>
<tr>
<td>H(_3)L + H(_2)A ⇌ H(_4)LA</td>
<td>3.59(3)</td>
<td>3.84(2)</td>
<td>3.50(2)</td>
<td>3.38(4)</td>
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<tr>
<td>H(_4)L + H(_2)A ⇌ H(_5)LA</td>
<td>3.64(5)</td>
<td>3.88(2)</td>
<td>3.59(3)</td>
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</tbody>
</table>

(a) Charges omitted. b) Values in parenthesis are standard deviations in the last significant figure.
Table S5. Thermodynamic data for ligands and neurotransmitters protonation and for the formation of L1 complexes with serotonin determined at 298.1 K in 0.15 mol·dm$^{-3}$ NaCl.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\log K$</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$T\Delta S^\circ$ (kJ/mol)</th>
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</thead>
<tbody>
<tr>
<td>L5</td>
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<td></td>
<td></td>
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<tr>
<td>$L + H \rightleftharpoons HL$</td>
<td>10.338(9)$^a$</td>
<td>-58.99(5)</td>
<td>-44.3(1)</td>
<td>14.7(1)</td>
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<tr>
<td>$HL + H \rightleftharpoons H_2L$</td>
<td>9.395(9)</td>
<td>-53.60(5)</td>
<td>-51.9(1)</td>
<td>1.7(1)</td>
</tr>
<tr>
<td>$H_2L + H \rightleftharpoons H_3L$</td>
<td>8.23(1)</td>
<td>-46.96(6)</td>
<td>-46.1(1)</td>
<td>0.9(1)</td>
</tr>
<tr>
<td>L4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L + H \rightleftharpoons HL$</td>
<td>10.006(4)</td>
<td>-57.09(2)</td>
<td>-40.4(2)</td>
<td>16.7(2)</td>
</tr>
<tr>
<td>$HL + H \rightleftharpoons H_2L$</td>
<td>8.746(3)</td>
<td>-49.90(2)</td>
<td>-48.4(2)</td>
<td>1.5(2)</td>
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<tr>
<td>$H_2L + H \rightleftharpoons H_3L$</td>
<td>7.368(4)</td>
<td>-42.04(2)</td>
<td>-46.6(2)</td>
<td>-4.6(2)</td>
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<tr>
<td>L3</td>
<td></td>
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</tr>
<tr>
<td>$L + H \rightleftharpoons HL$</td>
<td>10.153(9)</td>
<td>-57.93(5)</td>
<td>-37.6(1)</td>
<td>20.3(2)</td>
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<tr>
<td>$HL + H \rightleftharpoons H_2L$</td>
<td>9.473(9)</td>
<td>-54.05(5)</td>
<td>-37.5(1)</td>
<td>16.6(2)</td>
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<tr>
<td>$H_2L + H \rightleftharpoons H_3L$</td>
<td>8.516(8)</td>
<td>-48.59(5)</td>
<td>-43.0(1)</td>
<td>5.6(2)</td>
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<tr>
<td>$H_3L + H \rightleftharpoons H_4L$</td>
<td>7.341(9)</td>
<td>-41.89(5)</td>
<td>-46.1(1)</td>
<td>-4.2(2)</td>
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<tr>
<td>L2</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$L + H \rightleftharpoons HL$</td>
<td>10.13(2)</td>
<td>-57.8(1)</td>
<td>-36.7(1)</td>
<td>21.1(2)</td>
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<tr>
<td>$HL + H \rightleftharpoons H_2L$</td>
<td>9.50(1)</td>
<td>-54.20(6)</td>
<td>-36.0(1)</td>
<td>18.2(2)</td>
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<td>$H_2L + H \rightleftharpoons H_3L$</td>
<td>8.52(2)</td>
<td>-48.6(1)</td>
<td>-44.5(1)</td>
<td>4.1(2)</td>
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<tr>
<td>$H_3L + H \rightleftharpoons H_4L$</td>
<td>7.30(2)</td>
<td>-41.7(1)</td>
<td>-45.0(1)</td>
<td>-3.3(2)</td>
</tr>
<tr>
<td>L1</td>
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<tr>
<td>$L + H \rightleftharpoons HL$</td>
<td>9.93(1)</td>
<td>-56.66(6)</td>
<td>-39.02(5)</td>
<td>17.6(1)</td>
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<td>$HL + H \rightleftharpoons H_2L$</td>
<td>9.11(1)</td>
<td>-51.98(6)</td>
<td>-40.6(1)</td>
<td>11.4(2)</td>
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<td>$H_2L + H \rightleftharpoons H_3L$</td>
<td>7.92(1)</td>
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<td>2.1(2)</td>
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<td>$H_3L + H \rightleftharpoons H_4L$</td>
<td>6.76(1)</td>
<td>-38.57(6)</td>
<td>-38.5(1)</td>
<td>0.1(2)</td>
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<tr>
<td>Tyramine</td>
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<tr>
<td>$T + H \rightleftharpoons HT$</td>
<td>10.399(2)</td>
<td>-59.33(1)</td>
<td>-45.9(2)</td>
<td>13.4(2)</td>
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<tr>
<td>Reaction</td>
<td>$\Delta$ Energy</td>
<td>$\Delta$ Energy</td>
<td>$\Delta$ Energy</td>
<td>$\Delta$ Energy</td>
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<tr>
<td>----------</td>
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<tr>
<td>$HT + H \leftrightarrow H_2T$</td>
<td>9.333(2)</td>
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<td>-33.5(2)</td>
<td>18.8(2)</td>
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<tr>
<td>Serotonin</td>
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<td>$S + H \leftrightarrow HS$</td>
<td>10.765(4)</td>
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<td>-41.6(2)</td>
<td>19.0(2)</td>
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<td>$HS + H \leftrightarrow H_2S$</td>
<td>9.931(3)</td>
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<td>-44.0(2)</td>
<td>12.7(2)</td>
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<td>$L_5 + Serotonin$</td>
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<tr>
<td>$HS + HL \leftrightarrow HS(HL)$</td>
<td>2.89(2)</td>
<td>-16.5(1)</td>
<td>16.1(7)</td>
<td>32.6(8)</td>
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<tr>
<td>$H_2S + HL \leftrightarrow H_2S(HL)$</td>
<td>2.87(2)</td>
<td>-16.4(1)</td>
<td>23.1(7)</td>
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<tr>
<td>$H_2S + H_2L \leftrightarrow H_2S(H_2L)$</td>
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<td>-15.80(6)</td>
<td>27.6(8)</td>
<td>43.4(9)</td>
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<tr>
<td>$H_2S + H_3L \leftrightarrow H_3S(H_3L)$</td>
<td>2.76(1)</td>
<td>-15.75(6)</td>
<td>26.5(8)</td>
<td>42.3(9)</td>
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<tr>
<td>$L_4 + Tyramine$</td>
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<td></td>
</tr>
<tr>
<td>$HT + L \leftrightarrow HT(L)$</td>
<td>2.93(8)</td>
<td>-16.7(5)</td>
<td>20.5(4)</td>
<td>37.2(9)</td>
</tr>
<tr>
<td>$HT + HL \leftrightarrow HT(HL)$</td>
<td>3.18(3)</td>
<td>-18.1(2)</td>
<td>18.9(4)</td>
<td>37.0(6)</td>
</tr>
<tr>
<td>$H_2T + HL \leftrightarrow H_2T(HL)$</td>
<td>3.35(4)</td>
<td>-19.1(2)</td>
<td>15.0(4)</td>
<td>34.1(6)</td>
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<tr>
<td>$H_2T + H_2L \leftrightarrow H_2T(H_2L)$</td>
<td>3.35(3)</td>
<td>-19.1(2)</td>
<td>16.1(4)</td>
<td>35.2(6)</td>
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<tr>
<td>$H_2T + H_3L \leftrightarrow H_2T(H_3L)$</td>
<td>3.38(4)</td>
<td>-19.3(2)</td>
<td>15.1(4)</td>
<td>34.4(6)</td>
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<tr>
<td>$L_4 + Serotonin$</td>
<td></td>
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<tr>
<td>$HS + HL \leftrightarrow HS(HL)$</td>
<td>2.97(3)</td>
<td>-16.9(2)</td>
<td>12.5(4)</td>
<td>29.4(6)</td>
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<tr>
<td>$H_2S + HL \leftrightarrow H_2S(HL)$</td>
<td>2.73(2)</td>
<td>-15.6(1)</td>
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<td>25.6(5)</td>
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<tr>
<td>$H_2S + H_2L \leftrightarrow H_2S(H_2L)$</td>
<td>2.95(2)</td>
<td>-16.8(1)</td>
<td>9.7(4)</td>
<td>26.5(5)</td>
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<tr>
<td>$H_2S + H_3L \leftrightarrow H_2S(H_3L)$</td>
<td>3.21(2)</td>
<td>-18.3(1)</td>
<td>7.0 (4)</td>
<td>25.3(5)</td>
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<tr>
<td>$L_3 + Tyramine$</td>
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<tr>
<td>$HT + HL \leftrightarrow HT(HL)$</td>
<td>3.31(2)</td>
<td>-18.9(1)</td>
<td>10.2(4)</td>
<td>29.1(5)</td>
</tr>
<tr>
<td>$H_2T + HL \leftrightarrow H_2T(HL)$</td>
<td>3.61(2)</td>
<td>-20.6(1)</td>
<td>10.8(4)</td>
<td>31.4(5)</td>
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<tr>
<td>$H_2T + H_2L \leftrightarrow H_2T(H_2L)$</td>
<td>3.54(2)</td>
<td>-20.2(1)</td>
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<td>30.5(5)</td>
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<tr>
<td>$H_2T + H_3L \leftrightarrow H_2T(H_3L)$</td>
<td>3.50(2)</td>
<td>-20.0(1)</td>
<td>12.9(3)</td>
<td>32.9(4)</td>
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<tr>
<td>$H_2T + H_4L \leftrightarrow H_2T(H_4L)$</td>
<td>3.59(3)</td>
<td>-20.5(2)</td>
<td>13.9(3)</td>
<td>34.4(5)</td>
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<tr>
<td>$L_3 + Serotonin$</td>
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</tr>
<tr>
<td>Reaction</td>
<td>∆H (kJ/mol)</td>
<td>∆S (J/K/mol)</td>
<td>C (J/K/mol)</td>
<td>E (kJ/mol)</td>
</tr>
<tr>
<td>---------------------------------------------</td>
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<td>--------------</td>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td>( \text{HS} + \text{HL} \rightleftharpoons \text{HS(HL)} )</td>
<td>3.74(2)</td>
<td>-21.3(1)</td>
<td>22.0(5)</td>
<td>43.3(6)</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{HL} \rightleftharpoons \text{H}_2\text{S(HL)} )</td>
<td>3.57(2)</td>
<td>-20.4(1)</td>
<td>21.1(5)</td>
<td>41.5(6)</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{H}_2\text{L} \rightleftharpoons \text{H}_2\text{S(H}_2\text{L)} )</td>
<td>3.61(2)</td>
<td>-20.6(1)</td>
<td>16.3(5)</td>
<td>37.1(6)</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{H}_3\text{L} \rightleftharpoons \text{H}_2\text{S(H}_3\text{L)} )</td>
<td>3.53(3)</td>
<td>-20.1(2)</td>
<td>16.1(5)</td>
<td>36.2(7)</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{H}_4\text{L} \rightleftharpoons \text{H}_2\text{S(H}_4\text{L)} )</td>
<td>3.48(2)</td>
<td>-19.9(1)</td>
<td>17.2(5)</td>
<td>37.1(6)</td>
</tr>
</tbody>
</table>

**L2 + Tyramine**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>∆H (kJ/mol)</th>
<th>∆S (J/K/mol)</th>
<th>C (J/K/mol)</th>
<th>E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HT} + \text{HL} \rightleftharpoons \text{HT(HL)} )</td>
<td>3.68(2)</td>
<td>-21.0(1)</td>
<td>10.0(6)</td>
<td>31.0(7)</td>
</tr>
<tr>
<td>( \text{HT} + \text{H}_2\text{L} \rightleftharpoons \text{HT(H}_2\text{L)} )</td>
<td>3.73(2)</td>
<td>-21.3(1)</td>
<td>10.7(7)</td>
<td>32.0(8)</td>
</tr>
<tr>
<td>( \text{H}_2\text{T} + \text{H}_2\text{L} \rightleftharpoons \text{H}_2\text{T(H}_2\text{L)} )</td>
<td>3.83(2)</td>
<td>-21.9(1)</td>
<td>7.5(7)</td>
<td>29.4(8)</td>
</tr>
<tr>
<td>( \text{H}_2\text{T} + \text{H}_3\text{L} \rightleftharpoons \text{H}_2\text{T(H}_3\text{L)} )</td>
<td>3.84(2)</td>
<td>-21.9(1)</td>
<td>7.7(7)</td>
<td>29.6(8)</td>
</tr>
<tr>
<td>( \text{H}_2\text{T} + \text{H}_4\text{L} \rightleftharpoons \text{H}_2\text{T(H}_4\text{L)} )</td>
<td>3.88(2)</td>
<td>-22.1(1)</td>
<td>6.9(7)</td>
<td>29.0(8)</td>
</tr>
</tbody>
</table>

**L2 + Serotonin**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>∆H (kJ/mol)</th>
<th>∆S (J/K/mol)</th>
<th>C (J/K/mol)</th>
<th>E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HS} + \text{HL} \rightleftharpoons \text{HS(HL)} )</td>
<td>3.22(3)</td>
<td>-18.4(2)</td>
<td>14.4(5)</td>
<td>32.8(7)</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{HL} \rightleftharpoons \text{H}_2\text{S(HL)} )</td>
<td>3.00(3)</td>
<td>-17.1(2)</td>
<td>13.4(5)</td>
<td>30.5(7)</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{H}_2\text{L} \rightleftharpoons \text{H}_2\text{S(H}_2\text{L)} )</td>
<td>2.72(4)</td>
<td>-15.5(2)</td>
<td>5.8(4)</td>
<td>21.3(6)</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{H}_3\text{L} \rightleftharpoons \text{H}_2\text{S(H}_3\text{L)} )</td>
<td>2.32(7)</td>
<td>-13.2(4)</td>
<td>6.1(4)</td>
<td>19.3(6)</td>
</tr>
</tbody>
</table>

**L1 + Tyramine**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>∆H (kJ/mol)</th>
<th>∆S (J/K/mol)</th>
<th>C (J/K/mol)</th>
<th>E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HT} + \text{HL} \rightleftharpoons \text{HT(HL)} )</td>
<td>3.13(4)</td>
<td>-17.9(2)</td>
<td>16.7(5)</td>
<td>34.6(7)</td>
</tr>
<tr>
<td>( \text{H}_2\text{T} + \text{HL} \rightleftharpoons \text{H}_2\text{T(HL)} )</td>
<td>3.67(2)</td>
<td>-20.9(1)</td>
<td>15.7(4)</td>
<td>36.6(5)</td>
</tr>
<tr>
<td>( \text{H}_2\text{T} + \text{H}_2\text{L} \rightleftharpoons \text{H}_2\text{T(H}_2\text{L)} )</td>
<td>3.49(2)</td>
<td>-19.9(1)</td>
<td>19.5(5)</td>
<td>39.4(6)</td>
</tr>
<tr>
<td>( \text{H}_2\text{T} + \text{H}_3\text{L} \rightleftharpoons \text{H}_2\text{T(H}_3\text{L)} )</td>
<td>3.60(3)</td>
<td>-20.5(2)</td>
<td>19.0(4)</td>
<td>39.5(6)</td>
</tr>
<tr>
<td>( \text{H}_2\text{T} + \text{H}_4\text{L} \rightleftharpoons \text{H}_2\text{T(H}_4\text{L)} )</td>
<td>3.64(5)</td>
<td>-20.8(3)</td>
<td>17.4(5)</td>
<td>38.2(8)</td>
</tr>
</tbody>
</table>

**L1 + Serotonin**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>∆H (kJ/mol)</th>
<th>∆S (J/K/mol)</th>
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<th>E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HS} + \text{HL} \rightleftharpoons \text{HS(HL)} )</td>
<td>4.14(2)</td>
<td>-23.6(1)</td>
<td>20.9(4)</td>
<td>44.5(5)</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{HL} \rightleftharpoons \text{H}_2\text{S(HL)} )</td>
<td>4.23(1)</td>
<td>-24.14(6)</td>
<td>18.5(4)</td>
<td>42.6(5)</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{H}_2\text{L} \rightleftharpoons \text{H}_2\text{S(H}_2\text{L)} )</td>
<td>4.60(2)</td>
<td>-26.2(1)</td>
<td>16.0(4)</td>
<td>42.2(5)</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{H}_3\text{L} \rightleftharpoons \text{H}_2\text{S(H}_3\text{L)} )</td>
<td>4.94(2)</td>
<td>-28.2(1)</td>
<td>14.6(4)</td>
<td>42.8(5)</td>
</tr>
</tbody>
</table>
\[
\begin{array}{|c|c|c|c|c|}
\hline
H_2S + H_4L \rightleftharpoons H_2S(H_4L) & 5.14(3) & -29.3(2) & 7.9(4) & 37.2(6) \\
\hline
\end{array}
\]

(a) Charges omitted. (b) Obtained by means of potentiometric measurements. (c) Obtained by means of ITC. (d) Obtained from \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \). (e) Values in parenthesis are standard deviations in the last significant figure.

\[\text{i P. Gans, A. Sabatini and A. Vacca, Determination of equilibrium constants from spectrophotometric data obtained from solutions of known pH: The program pHab. Annali di Chimica, 1999, 89, 45-49}\]