

# Cyanide-Catalyzed Cyclizations via Aldimine Coupling

B. Jesse E. Reich, Aaron K. Justice, Brittany T. Beckstead, Joseph H. Reibenspies,  
and Stephen A. Miller\*

*Department of Chemistry, Texas A&M University  
College Station, TX 77843-3255*

## Supporting Information

**Supporting Information Available:** Experimental procedures and compound characterization data, including X-ray crystallographic data for 5,6-di-(2-hydroxyphenyl)-2,3-dihdropyrazine and 2,3-di-(2-hydroxyphenyl)-quinoxaline.

### Table of Contents

General Considerations and Instrumentation.....	S2
Preparation of Dialdimine Substrates .....	S2
Cyanide-catalyzed Cyclizations and Oligomerizations .....	S3
Substrate and Product Summary .....	S6
NMR Analysis of Turnover Numbers .....	S7
$^1\text{H}$ NMR Spectra .....	S9
X-Ray Structure Data for 5,6-di-(2-hydroxyphenyl)-2,3-dihdropyrazine .....	S15
X-Ray Structure Data for 2,3-di-(2-hydroxyphenyl)-quinoxaline .....	S18

**General Considerations and Instrumentation.** Granular sodium cyanide was used as received from Mallinckrodt. X-ray crystallographic data were obtained on a Bruker SMART 1000 three-circle diffractometer operating at 50 kV and 40 mA, Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) with a graphite monochromator and a CCD-PXL-KAF2 detector.

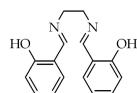
**Preparation of Dialdimine Substrates.** Three general procedures were utilized to synthesize the symmetrical dialdimine substrates, all of which are known compounds (See the following Substrate and Product Summary).

**Method A.** 200 mmol of an aldehyde were dissolved in 80-200 mL of water. To this, 100 mmol of liquid diamine were added and the reaction was shaken for 16 hours. In the case of solid formation, the solid was isolated by filtration, washed with 200-300 mL of water, washed with 100 mL of hexanes, and dried *in vacuo*. All yields were greater than 90% and often analytically pure (small concentrations of starting aldehyde could be detected in some products). In the case of a liquid product, a dichloromethane/water extraction was performed. The organic layer was dried over magnesium sulfate and filtered. The dichloromethane was removed by rotary evaporation and the resulting solid was dried *in vacuo* to provide an analytically pure solid in greater than 90% yield.

**Method B.** 200 mmol of an aldehyde were dissolved in 80-200 mL of methanol. To this, 100 mmol of liquid diamine were added and the reaction was shaken for 16 hours. In the case of solid formation, the solid was isolated by filtration, washed with 100-200 mL of alcohol, and dried *in vacuo*. All yields were greater than 90% and often analytically pure (small concentrations of starting aldehyde could be detected in some products). In the case of a liquid product, the solvent was removed *in vacuo* and a dichloromethane/water extraction was performed. The organic layer was dried over magnesium sulfate and filtered. The dichloromethane was removed by rotary evaporation and the resulting solid was dried *in vacuo* to provide an analytically pure solid in greater than 90% yield.

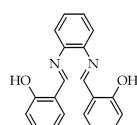
**Method C.** 200 mmol of an aldehyde, 100 mmol of a diamine, 0.10 g (0.52 mmol) of *p*-toluenesulfonic acid, and 300 mL of toluene were combined. A Dean-Stark trap and a condenser were attached to the flask and the reaction was heated and stirred at reflux. When the expected 3.6 mL of water were isolated, the toluene was removed by rotary evaporation and the resulting solid was triturated in 200 mL of hexanes. The solid was isolated by filtration and dried *in vacuo* to provide the product in greater than 90% yield.

**N,N'-bis(salicylidene)-ethane-1,2-diamine (salen).** Method A.



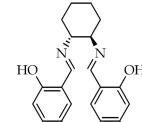
$^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  -1.81 (s, 2H), 3.97 (s, 4H), 6.87 (t, 2H,  $^3J_{\text{HH}} = 7.4 \text{ Hz}$ ), 6.95 (d, 2H,  $^3J_{\text{HH}} = 8.0 \text{ Hz}$ ), 7.24 (d, 2H,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ ), 7.31 (t, 2H,  $^3J_{\text{HH}} = 6.6 \text{ Hz}$ ), 8.37 (s, 2H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  60.0, 117.2, 118.83, 118.88, 131.7, 132.6, 161.2, 166.7. MS (ESI)  $m/z = 269$  [M+H]<sup>+</sup>. C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> (268.31).

**N,N'-bis(salicylidene)-*o*-phenylenediamine (salophen)**  
Method B.



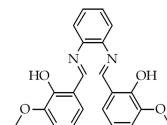
$^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  -1.90 (s, 2H), 6.94 (t, 2H,  $^3J_{\text{HH}} = 7.5 \text{ Hz}$ ), 7.07 (d, 2H,  $^3J_{\text{HH}} = 7.5 \text{ Hz}$ ), 7.24 (m, 2H), 7.35 (m, 2H), 7.40 (m, 4H), 8.64 (s, 2H).  $^{13}\text{C}$  NMR:  $\delta$  117.6, 119.1, 119.4, 119.8, 127.9, 132.5, 133.5, 142.6, 161.5, 163.8. MS (ESI)  $m/z = 317$  [M+H]<sup>+</sup>. C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> (316.35).

**(+/-)-N,N'-bis(salicylidene)-*trans*-1,2-diaminocyclohexane.**  
Method A.



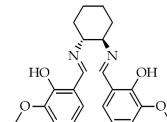
$^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  -1.6 (s, 2H), 1.46 (m, 2H), 1.78 (m, 2H), 1.88 (m, 4H), 3.30 (m, 2H), 6.82 (t, 2H,  $^3J_{\text{HH}} = 7.2 \text{ Hz}$ ), 6.95 (d, 2H,  $^3J_{\text{HH}} = 8.4 \text{ Hz}$ ), 7.18 (d, 2H,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ ), 7.27 (m, 2H), 8.28 (s, 2H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  24.4, 33.3, 72.8, 117.1, 118.3, 118.8, 131.8, 132.5, 161.3, 165.0. MS (ESI)  $m/z = 323$  [M+H]<sup>+</sup>. C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> (322.40).

**N,N'-bis(*o*-vanillidene)-*o*-phenylenediamine.** Method B.



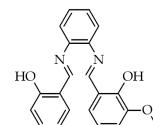
$^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  -1.8 (s, 2H), 3.88, (s, 6H, methyl-H), 6.85 (t, 2H,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ ), 6.99 (m, 4H), 7.19 (m, 2H), 7.32 (m, 2H), 8.60 (s, 2H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  56.3, 115.2, 118.7, 119.3, 120.4, 124.1, 127.8, 142.6, 148.7, 151.7, 164.4. MS (ESI)  $m/z = 377$  [M+H]<sup>+</sup>. C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub> (376.41).

**(+/-)-N,N'-bis(*o*-vanillidene)-*trans*-1,2-diaminocyclohexane.**  
Method B.



$^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  -1.16 (s, 2H), 1.48 (m, 2H), 1.71 (m, 2H), 1.90 (m, 4H), 3.31 (m, 2H), 3.86 (s, 6H), 6.71 (t, 2H,  $^3J_{\text{HH}} = 7.5 \text{ Hz}$ ), 6.78 (d, 2H,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ ), 6.85 (d, 2H,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ ), 8.24 (s, 2H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>): 24.2, 33.1, 56.1, 72.5, 113.9, 118.0, 118.5, 123.3, 148.4, 151.7, 164.9. MS (ESI)  $m/z = 383$  [M+H]<sup>+</sup>. C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub> (382.45).

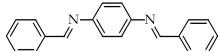
**N-(salicylidene)-N'-(*o*-vanillidene)-*o*-phenylenediamine.**



4.32g (40 mmol) of *o*-phenylene diamine were dissolved into 400 mL of pure ethanol and cooled to 0°C in an ice water bath. An addition funnel containing 4.88g (40 mmol) of salicylaldehyde dissolved in 200 mL of ethanol was attached and the dropwise addition was performed over five hours. When the addition was complete the vessel was allowed to stir and warm for one hour. The addition funnel was removed and the solution filtered. To the filtrate 6.09 g (40 mmol) of *o*-vanillin was added and the mixture was shaken overnight. The flask was then heated to reflux and triturated for twenty minutes to yield a first crop of 5.73 grams of bright burnt-orange powder by filtration. The filtrate was cooled to 0°C and filtration yielded 5.36g of orange-red crystals as the

second crop. Yield for both crops: 80.0%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -2.08 (s, 0.9H), -1.97 (s, 0.1H), -1.85 (s, 0.1H), -1.77 (s, 0.9H), 3.88 (s, 0.3H), 3.89 (s, 2.7H), 6.93 (m, 5H), 7.21 (m, 2H), 7.34 (m, 4H), 8.628 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  56.36, 115.2, 117.8, 118.7, 119.1, 119.4, 120.0, 120.2, 120.5, 120.6, 124.1, 127.8, 127.9, 132.6, 133.6, 142.7, 148.8, 151.8, 161.6, 164.2, 164.4. MS (ESI)  $m/z$  = 347 [M+H] $^+$  369 [M+Na] $^+$ .  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3$  (346.38).

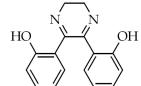
***N,N'*-bis(benzylidene)-*p*-phenylenediamine.** Method C.



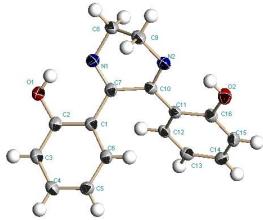
$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.31 (s, 4H), 7.49 (m, 6H), 7.94 (m, 4H), 8.54 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  122.2, 129.1, 129.1, 131.7, 136.5, 150.2, 160.0. MS (ESI)  $m/z$  = 285 [M+H] $^+$ .  $\text{C}_{20}\text{H}_{16}\text{N}_2$  (284.35).

**Cyanide-catalyzed Cyclizations and Oligomerizations.** Eight cyclized products were characterized by X-ray crystallography; thermal ellipsoid diagrams (with 50% probability) and crystallographic summaries are included. Complete crystallographic data, where absent, will be reported elsewhere.

**5,6-di-(2-hydroxyphenyl)-2,3-dihydropyrazine.**

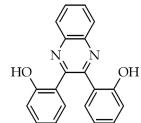


A flask was charged with 12.72 g (47.4 mmol) of *N,N'*-bis(salicylidene)-ethane-1,2-diamine, 2.00 g of NaCN (40.8 mmol) and 100 mL of *N,N*-dimethylformamide. This was allowed to stir for 120 hours and then poured into an ice water bath. The resulting orange solid was isolated by filtration, dissolved into hot ethyl acetate, and filtered. Slow evaporation of the ethyl acetate solution provided 6.112 grams (48.1%) of orange-red crystal blocks (2mm x 2mm x 2mm).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -1.87 (s, 2H), 3.70 (broad s, 4H), 6.64 (t 2H,  $^3J_{\text{HH}} = 7.7$ , 7.04 (m, 4H), 7.29 (t, 2H,  $^3J_{\text{HH}} = 9.0$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  44.7, 117.96, 118.04, 118.3, 131.3, 132.8, 161.0, 162.4. MS (ESI)  $m/z$  = 267 [M+H] $^+$ .  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$  (266.29). X-ray crystallography (SM08):

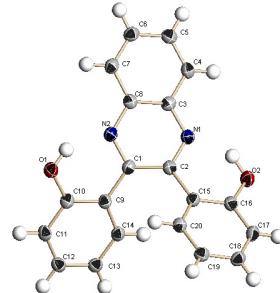


Orange-red blocks were grown by slow evaporation of an ethyl acetate solution. Crystal data: triclinic,  $P-1$ ,  $a = 5.8600(7)$  Å,  $b = 8.4944(10)$  Å,  $c = 13.4511(17)$  Å,  $\alpha = 101.721(2)^\circ$ ,  $\beta = 98.011(2)^\circ$ ,  $\gamma = 99.562(2)^\circ$ ,  $V = 636.01(13)$  Å $^3$ ,  $Z = 2$ ,  $T = 110(2)$  K,  $R_1$  (on  $\text{F}_0$ ) = 0.0602,  $wR_2$  (on  $\text{F}_0^2$ ) = 0.1569, GOF = 1.089 for 184 parameters and 2189 unique data.

**2,3-di-(2-hydroxyphenyl)-quinoxaline.**

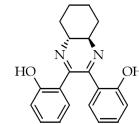


A flask was charged with 8.00 g (25.3 mmol) of *N,N'*-bis(salicylidene)-*o*-phenylenediamine, 0.496 g (10.1 mmol) of NaCN and 110 mL of *N,N*-dimethylformamide. This was allowed to stir for 48 hours and then poured into ice water. The resulting yellow solid was isolated by filtration, dissolved in dichloromethane, and dried over magnesium sulfate. Filtration and *in vacuo* drying provided 7.00 g (87.5%) of a yellow powder. The product can be recrystallized from acetone, toluene or ethyl acetate.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.69 (m, 2H), 7.15 (m, 2H), 7.29 (m, 4H), 7.80 (m, 2H), 8.05 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  118.6, 119.3, 120.7, 127.9, 131.0, 131.8, 132.2, 137.9, 151.7, 157.0. MS (ESI)  $m/z$  = 315 [M+H] $^+$ .  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2$  (314.34). X-ray crystallography (SM12):

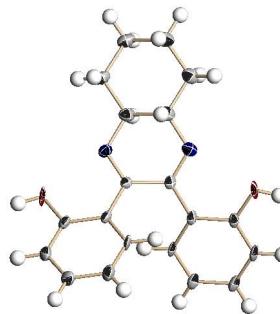


Yellow plates were grown by slow evaporation of an acetone solution. Crystal data: triclinic,  $P-1$ ,  $a = 5.9430(9)$  Å,  $b = 8.6856(13)$  Å,  $c = 14.988(2)$  Å,  $\alpha = 74.255(2)^\circ$ ,  $\beta = 81.050(2)^\circ$ ,  $\gamma = 83.614(2)^\circ$ ,  $V = 733.64(19)$  Å $^3$ ,  $Z = 2$ ,  $T = 110(2)$  K,  $R_1$  (on  $\text{F}_0$ ) = 0.0572,  $wR_2$  (on  $\text{F}_0^2$ ) = 0.1430, GOF = 1.091 for 225 parameters and 2472 unique data.

**(+/-)-2,3-di-(2-hydroxyphenyl)-*trans*-4a,5,6,7,8,8a-hexahydroquinoxaline.**

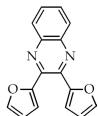


A flask was charged with 1.60 (4.99 mmol) grams of (+/-)-*N,N'*-bis(salicylidene)-*trans*-1,2-diaminocyclohexane, 0.245 g (5.00 mmol) of NaCN, 15 mL of methanol, and the vessel was heated to reflux. Heat was removed after 24 hours, and the solvent was removed by rotary evaporation. The resulting solid was washed with dichloromethane and the washings were combined, gravity filtered, and then dried *in vacuo* to provide 0.94 g (58.8%) of a red powder. Single crystals suitable for single crystal X-Ray diffraction can be grown by slow evaporation from dichloromethane.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -1.68 (s, 2H), 1.44 (m, 2H), 1.62 (m, 2H), 1.92 (m, 2H), 2.47 (m, 2H), 2.94 (m, 2H), 6.64 (t, 2H,  $^3J_{\text{HH}} = 7.7$  Hz), 7.05 (d, 4H,  $^3J_{\text{HH}} = 8.7$  Hz), 7.29, (t, 2H,  $^3J_{\text{HH}} = 8.7$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  25.1, 32.8, 58.7, 117.8, 118.0, 118.3, 131.3, 132.7, 161.1, 161.6. MS (ESI)  $m/z$  = 321 [M+H] $^+$ .  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2$  (320.39). X-ray crystallography (SM09):

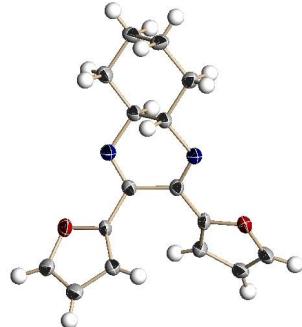


Orange-red blocks were grown by slow evaporation of a dichloromethane solution. Crystal data: monoclinic,  $Pn$ ,  $a = 8.375(4)$  Å,  $b = 6.257(3)$  Å,  $c = 15.609(8)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 100.709(9)^\circ$ ,  $\gamma = 90^\circ$ .  $V = 803.7(7)$  Å $^3$ ,  $Z = 2$ ,  $T = 110(2)$  K,  $R_1$  (on  $F_0$ ) = 0.0801,  $wR_2$  (on  $F_0^2$ ) = 0.1201, GOF = 1.040 for 217 parameters and 2658 unique data.

### 2,3-di-(2-furyl)-quinoxaline.

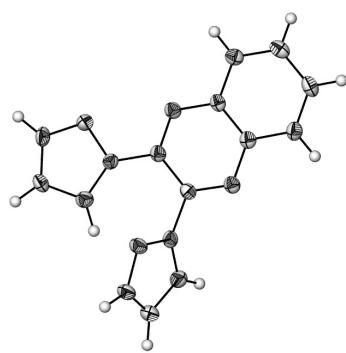
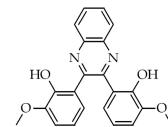


A flask was charged with 1.92 g (20.0 mmol) of 2-furaldehyde, 1.08 g (10.0 mmol) of *o*-phenylenediamine, and 50 mL of *N,N*-dimethylformamide. The solution was allowed to stir for 24 hours at which point 0.50 g (10 mmol) of sodium cyanide were added and the solution was allowed to stir for an additional 48 hours. The solution was poured into an ice water bath and the solid was collected by filtration. The solid was dissolved in dichloromethane, dried over magnesium sulfate, and filtered; solvent from the filtrate was removed by rotary evaporation. The resulting solid was dried *in vacuo* and then recrystallized from methanol, providing 1.38 g (52.8%) of tan needles.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.57 (m, 2H), 6.67 (d, 2H,  $^3J_{\text{HH}} = 6.6$  Hz), 7.64 (d, 2H,  $^3J_{\text{HH}} = 3.3$  Hz), 7.76 (m, 2H), 8.15 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  112.1, 113.2, 129.3, 130.6, 140.8, 142.9, 144.5, 151.9. MS (ESI)  $m/z = 263$  [M+H] $^+$ .  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$  (262.23). X-ray crystallography (SM20):



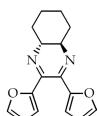
Green plates were grown by slow evaporation of a methanol solution. Crystal data: monoclinic,  $C2k$ ,  $a = 14.140(7)$  Å,  $b = 10.157(5)$  Å,  $c = 9.583(5)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 94.221(9)^\circ$ ,  $\gamma = 90^\circ$ .  $V = 1372.7(12)$  Å $^3$ ,  $Z = 4$ ,  $T = 273(2)$  K,  $R_1$  (on  $F_0$ ) = 0.0555,  $wR_2$  (on  $F_0^2$ ) = 0.1302, GOF = 1.064 for 91 parameters and 991 unique data.

### 2,3-di-(2-hydroxy-3-methoxyphenyl)-quinoxaline.

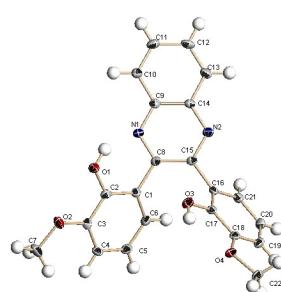


Tan needles were grown by slow evaporation of a methanol solution. Crystal data: orthorhombic,  $Pna2_1$ ,  $a = 15623(2)$  Å,  $b = 16.870(2)$  Å,  $c = 4.6291(6)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ .  $V = 1220.0(3)$  Å $^3$ ,  $Z = 4$ ,  $T = 110(2)$  K,  $R_1$  (on  $F_0$ ) = 0.0545,  $wR_2$  (on  $F_0^2$ ) = 0.1258, GOF = 1.007 for 181 parameters and 2358 unique data.

### (+/-)-2,3-di-(2-furyl)-*trans*-4a,5,6,7,8a-hexahydroquinoxaline.



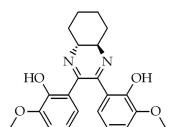
A flask was charged with 1.92 g (20.0 mmol) of 2-furaldehyde, 1.14 g (10.0 mmol) of (+/-)-*trans*-1,2-diaminocyclohexane, and 50 mL of *N,N*-dimethylformamide. The solution was allowed to stir for 24 hours at which point 0.50 g (10 mmol) of sodium cyanide were added and the solution was allowed to stir for an additional 48 hours. The solution was poured into an ice water bath and the solid was collected by suction filtration. The solid was dissolved in dichloromethane, dried over magnesium sulfate, and filtered; solvent from the filtrate was removed by rotary



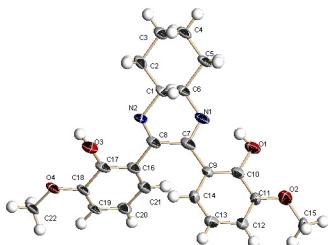
Tan needles were grown by slow evaporation of a methanol solution. Crystal data: monoclinic,  $P2_1/n$ ,  $a = 14.0608(14)$  Å,  $b = 8.0440(8)$  Å,  $c = 15.6788 (16)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 102.031(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1734.4(3)$  Å $^3$ ,  $Z = 4$ ,  $T = 110(2)$  K,  $R_1$  (on  $F_0$ ) = 0.0537,

$wR_2$  (on  $F_0^2$ ) = 0.1344, GOF = 1.002 for 262 parameters and 4143 unique data.

**(+/-)-2,3-di-(2-hydroxy-3-methoxyphenyl)-trans-4a,5,6,7,8a-hexahydroquinoxaline.**

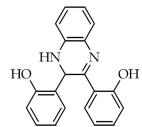


In a flask 3.82 g (10.0 mmol) of (+/-)-*N,N*-bis(*o*-vanillinidene)-*trans*-1,2-diaminocyclohexane and 0.50 g (10 mmol) of sodium cyanide were dissolved in 50 mL of methanol. The solution was heated to reflux and allowed to stir for 48 hours. Heat was removed and methanol was removed by rotary evaporation. 50 mL of water and 50 mL of dichloromethane were added to the flask. The contents were poured into a separatory funnel and the organic layer was removed. The remaining aqueous layer was washed with dichloromethane and all of the organic extracts were combined, washed with water, and dried over magnesium sulfate. This was filtered and the solvent was removed from the filtrate by rotary evaporation. The resulting orange-red solid was dried *in vacuo*: 1.56 g (41.1%). Single crystals can be grown from methanol, ethanol, or ethyl acetate.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  -1.32 (broad s, 2H), 1.42 (m, 2H), 1.60 (m, 2H), 1.90 (m, 2H), 2.45 (d, 2H,  $^3J_{HH}$  = 13.6 Hz), 2.95 (m, 2H), 3.9 (s, 6H), 6.58 (t, 2H,  $^3J_{HH}$  = 8.1 Hz), 6.66 (d, 2H,  $^3J_{HH}$  = 8.0 Hz), 6.89 (d, 2H,  $^3J_{HH}$  = 8.1 Hz).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  25.0, 32.7, 56.3, 58.6, 113.9, 117.2, 117.8, 122.9, 149.1, 151.9, 161.8 MS (ESI)  $m/z$  = 381 [M+H] $^+$ .  $C_{22}H_{18}N_2O_4$  (380.44). X-ray crystallography (SM27):



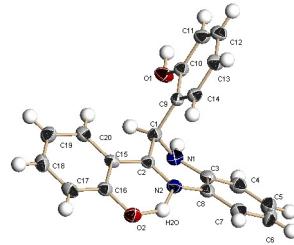
Orange needles were grown by slow evaporation of an ethyl acetate solution. Crystal data: monoclinic,  $P2(1)$ ,  $a$  = 6.817(5) Å,  $b$  = 17.352(5) Å,  $c$  = 8.606(5) Å,  $\alpha$  = 90.000(5) $^\circ$ ,  $\beta$  = 112.182(5) $^\circ$ ,  $\gamma$  = 90.000(5) $^\circ$ ,  $V$  = 942.6(9) Å $^3$ ,  $Z$  = 2,  $T$  = 110(2) K,  $R_1$  (on  $F_0$ ) = 0.0801,  $wR_2$  (on  $F_0^2$ ) = 0.1685, GOF = 1.061 for 257 parameters and 2068 unique data.

**(+/-)-2,3-di-(2-hydroxyphenyl)-1,2-dihydroquinoxaline.**



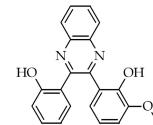
A flask was charged with 11.60 g (40.8 mmol) of *N,N*-bis(salicylidene)-*o*-phenylenediamine, 2.00 g (40.8 mmol) of sodium cyanide, 1.50 g (4.06 mmol) of tetra-*n*-butylammonium iodide, 100 mL of dichloromethane, and 100 mL of water. The reaction was refluxed for 64 hours. The solid that formed at the interface of the two phases was isolated by suction filtration and dried *in vacuo* to yield 6.50 g (56.0%) of product. Single crystals can be grown by slow evaporation of a toluene solution.  $^1H$  NMR

(acetone- $d_6$ ):  $\delta$  0.21 (s, 1H), 2.85 (broad s, 1H), 6.11 (broad s, 1H), 6.34 (s, 1H), 6.61-6.78 (m, 4H) 6.91-7.10 (m, 5H), 7.27-7.32 (m, 2H), 7.47 (d, 1H,  $^3J_{HH}$  = 8.1 Hz)  $^{13}C$  NMR (acetone- $d_6$ ):  $\delta$  48.0, 115.7, 117.0, 119.0, 119.3, 119.6, 121.2, 126.6, 127.2, 127.8, 129.1, 129.1, 130.3, 130.7, 131.4, 133.8, 138.2, 154.4, 163.0, 163.8. MS (ESI)  $m/z$  = 317 [M+H] $^+$ .  $C_{20}H_{16}N_2O_2$  (316.35). X-ray crystallography (SM11):



Orange-red blocks were grown by slow evaporation of a hot toluene solution. Crystal data: monoclinic,  $P2_1/n$ ,  $a$  = 9.708(2) Å,  $b$  = 15.970(4) Å,  $c$  = 11.254(3) Å,  $\alpha$  = 90 $^\circ$ ,  $\beta$  = 115.496(3) $^\circ$ ,  $\gamma$  = 90 $^\circ$ ,  $V$  = 1574.9(6) Å $^3$ ,  $Z$  = 4,  $T$  = 110(2) K,  $R_1$  (on  $F_0$ ) = 0.0557,  $wR_2$  (on  $F_0^2$ ) = 0.1015, GOF = 1.056 for 229 parameters and 3553 unique data.

**2-(2-hydroxyphenyl)-3-(2-hydroxy-3-methoxyphenyl)-quinoxaline.**



A flask was charged with 3.00 g (8.66 mmol) of *N*-(salicylidene)-*N'*-(*o*-vanillinidene)-*o*-phenylenediamine, 0.43 g (8.66 mmol) of NaCN, and 50 ml of *N,N*-dimethylformamide. This was allowed to stir at 70°C for 24 hours. The solution was then poured into 200 ml of ice water. The powder was collected by filtration and dried *in vacuo* to yield 1.96g of a tan powder (65.8%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  3.93 (s, 3H), 6.61 (t, 1H,  $^3J_{HH}$  = 7.8) 6.82 (t, 1H,  $^3J_{HH}$  = 8.1), 6.93 (d, 1H,  $^3J_{HH}$  = 7.2), 7.01 (d, 2H,  $^3J_{HH}$  = 7.8), 7.10 (d, 1H,  $^3J_{HH}$  = 8.1), 7.24 (m, 2H), 7.78 (m, 2H), 8.06 (m, 2H), 8.94 (bs, 1H), 11.95 (bs, 1H).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  56.4, 112.7, 118.3, 119.0, 119.8, 120.6, 123.0, 123.8, 127.8, 128.7, 130.7, 130.8, 131.0, 132.0, 138.0, 139.2, 145.6, 148.4, 151.6, 152.3, 158.2. MS (ESI)  $m/z$  = 345 [M+H] $^+$ .  $C_{21}H_{16}N_2O_3$  (344.37).

**Oligomerization of *N,N*-bis(benzylidene)-*p*-phenylenediamine.** A flask was charged with 8.53 g (30.0 mmol) of *N,N*-bis(benzylidene)-*p*-phenylenediamine, 1.44 g (29.4 mmol) of sodium cyanide, 80 mL of *N,N*-dimethylformamide, and was heated to 145° C. The reaction was stirred for two days and then heat was removed. The solution was poured into an ice water bath and the resulting solid was isolated by filtration. The solid was dissolved in 1,2-dichloroethane, heated to reflux, dried over magnesium sulfate, and filtered while hot; solvent from the filtrate was removed by rotary evaporation. The resulting solid was dried *in vacuo* to yield 3.60 g (42.2%) of a red powder. Integral comparison between aldehydic (2.81) and aromatic (85.43) hydrogens in the  $^1H$  NMR spectrum indicates the average degree of polymerization to be 4.34 (85.43/2.81 = 30.40. There is a 7:1 ratio of aldehydic to aromatic hydrogens in the starting material. 30.40/7 = 4.34).

**Substrate and Product Summary** (Structure of all eight symmetrical, monomeric products confirmed by X-ray crystallography.)

Substrate	Substrate Name Lab Notebook#, CAS#, Reference		Substrate, g	NaCN, mol% NaCN, g		Product	Product Name Lab Notebook#, CAS#, Reference		Yield, isolated % Yield, g
	<i>N,N'</i> -bis(salicylidene)-ethane-1,2-diamine BJR-I-72, [94-93-9], (1)		12.72	86% 2.00 g			5,6-di-(2-hydroxyphenyl)-2,3-dihydropyrazine BJR-I-82, no CAS#		
	<i>N,N'</i> -bis(salicylidene)- <i>o</i> -phenylenediamine BJR-I-155, [3946-91-6], (2)		8.00	40% 0.496 g			2,3-di-(2-hydroxyphenyl)-quinoxaline BJR-I-172, [4196-27-4], (10)		
	(+/-)- <i>N,N'</i> -bis(salicylidene)- <i>trans</i> -1,2-diaminocyclohexane BJR-I-95, (R,R): [3187-83-5], (S,S): [41013-28-9], (3)		1.60	100% 0.245 g			(+/-)-2,3-di-(2-hydroxyphenyl)- <i>trans</i> -4a,5,6,7,8,8a-hexahydroquinoxaline BJR-I-157, no CAS#		
	<i>N,N'</i> -bis(furylidene)- <i>o</i> -phenylenediamine [15419-92-8], (4)		2.62*	100% 0.50 g			2,3-di-(2-furyl)-quinoxaline AKJ-I-132, [57490-73-0], (11)		
	(+/-)- <i>N,N'</i> -bis(furylidene)- <i>trans</i> -1,2-diaminocyclohexane [143283-95-8], (5)		2.68*	100% 0.50 g			(+/-)-2,3-di-(2-furyl)- <i>trans</i> -4a,5,6,7,8,8a-hexahydroquinoxaline AKJ-I-138, (R,R): [171029-70-2], (S,S): [171029-71-3], (12)		
	<i>N,N'</i> -bis( <i>o</i> -vanillidene)- <i>o</i> -phenylenediamine AKJ-I-75, [10319-00-3], (6)		3.76	100% 0.50 g			2,3-di-(2-hydroxy-3-methoxyphenyl)-quinoxaline AKJ-I-83, no CAS#		
	(+/-)- <i>N,N'</i> -bis( <i>o</i> -vanillidene)- <i>trans</i> -1,2-diaminocyclohexane BJR-I-98, (R,R): [431878-13-6] (S,S): [177898-70-3], (7)		3.82	100% 0.50 g			(+/-)-2,3-di-(2-hydroxy-3-methoxyphenyl)- <i>trans</i> -4a,5,6,7,8,8a-hexahydroquinoxaline AKJ-I-100, no CAS#		
	<i>N,N'</i> -bis(salicylidene)- <i>o</i> -phenylenediamine BJR-I-155, [3946-91-6], (2)		11.60	100% 2.00 g 10% Bu <sub>4</sub> Ni			(+/-)-2,3-di-(2-hydroxyphenyl)-1,2-dihydroquinoxaline BB-I-18, no CAS#		
	<i>N</i> -(salicylidene)- <i>N'</i> -( <i>o</i> -vanillidene)- <i>o</i> -phenylenediamine BJR-II-114, no CAS# (8)		3.00	100% 0.43 g			2-(2-hydroxyphenyl)-3-(2-hydroxy-3-methoxyphenyl)-quinoxaline BJR-II-115, no CAS#		
	<i>N,N'</i> -bis(benzylidene)- <i>p</i> -phenylenediamine BJR-I-126, [797-20-6], (9)		8.53	100% 1.44 g		oligomers DP = 4.34	BJR-I-128, no CAS#		
			48 h	64 h					
			145°	70°					

(\*) These two substrates were not isolated prior to cyclization; the substrate masses represent the theoretical yield of *in situ* formation.

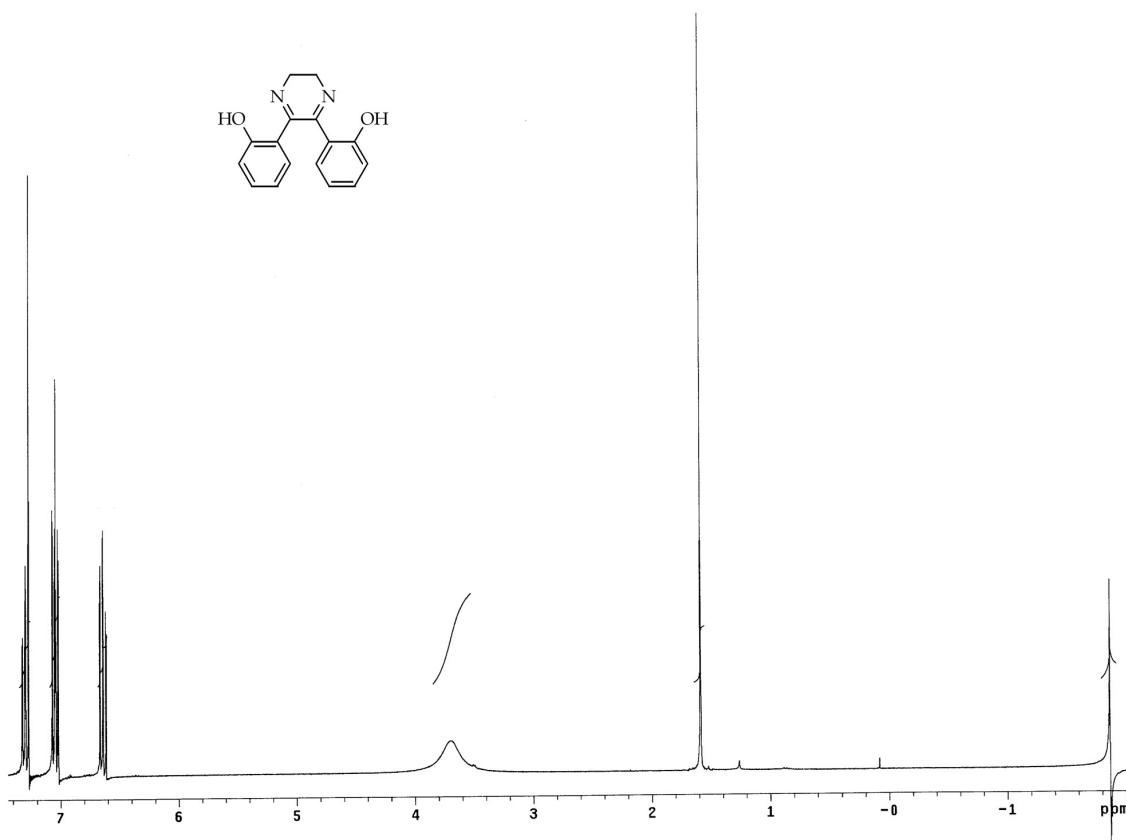
- (1) Bresciani, P. N.; Calligaris, M.; Nardin, G.; Randaccio, L. *Acta Cryst., Sect. B* **1978**, *B34*(4), 1360-1363.
- (2) Heagle, E.; *Ber.* **1892**, 26, 2755.
- (3) McAllister, R. M.; Weber, J. H. *J. Organomet. Chem.* **1974**, *77*(1), 91-105.
- (4) Mukhopadhyay, M.; Reddy, M. M.; Maikap, G. C.; Iqbal, J. *J. Org. Chem.* **1995**, *60*, 2670-2676.
- (5) Weers, J. J.; O'Brien, T. J.; Thomasson, C. E. *European Patent* 475,641, **1992**.
- (6) Dey, D. K.; Saha, M. K.; Das, M. K.; Bhartiya, N.; Bansal, R. K.; Rosair, G.; Mitra, S. *Polyhedron* **1999**, *18*(20), 2687-2696.
- (7) (a) Lin, M.-H.; RajanBabu, T. V. *Org. Lett.* **2002**, *4*, 1607-1610. (b) Torayama, H.; Nishide, T.; Asada, H.; Fujiwara, M.; Matsushita, T. *Chem. Lett.* **1996**, *5*, 387-388.
- (8) This unsymmetrical dialdimine was prepared by modification of a literature procedure: Boghaei, D. M.; Mohebi, S. *Tetrahedron* **2002**, *58*(26), 5357-5366.
- (9) (a) Landenburg, A.; *Ber. 1878*, *11*, 599. (b) Hodgkin, J. H.; Heller, J. *Macromolecules* **1969**, *2*, 556-558.
- (10) Tanaka, S.; Yokoyama, K.; Takashima, M. *Japanese Patent* 40,012,294, **1965**.
- (11) Bost, R. W.; Towell, E. E. *J. Am. Chem. Soc.* **1948**, *70*, 903-905.
- (12) Jimeno, M. L.; de Paz, J. L. G.; Rodriguez, J.; Rodriguez, M.; Ochoa, C. *Anales de Quimica* **1994**, *90*(7-8), 423-431.

**NMR Analysis of Turnover Numbers.** General Procedure: In a 250 mL round bottom flask, 10.0 mmol of the desired substrate and 1.0 mmol of NaCN (0.050g, **10 mol%**) were dissolved in 50 mL of *N,N*-dimethylformamide. The reactions were then allowed to stir at room temperature. At the specified times, 2 mL aliquots were removed and placed into a separate flask; solvent was removed by rotary evaporation and high vacuum before the addition of CDCl<sub>3</sub> and <sup>1</sup>H NMR analysis.

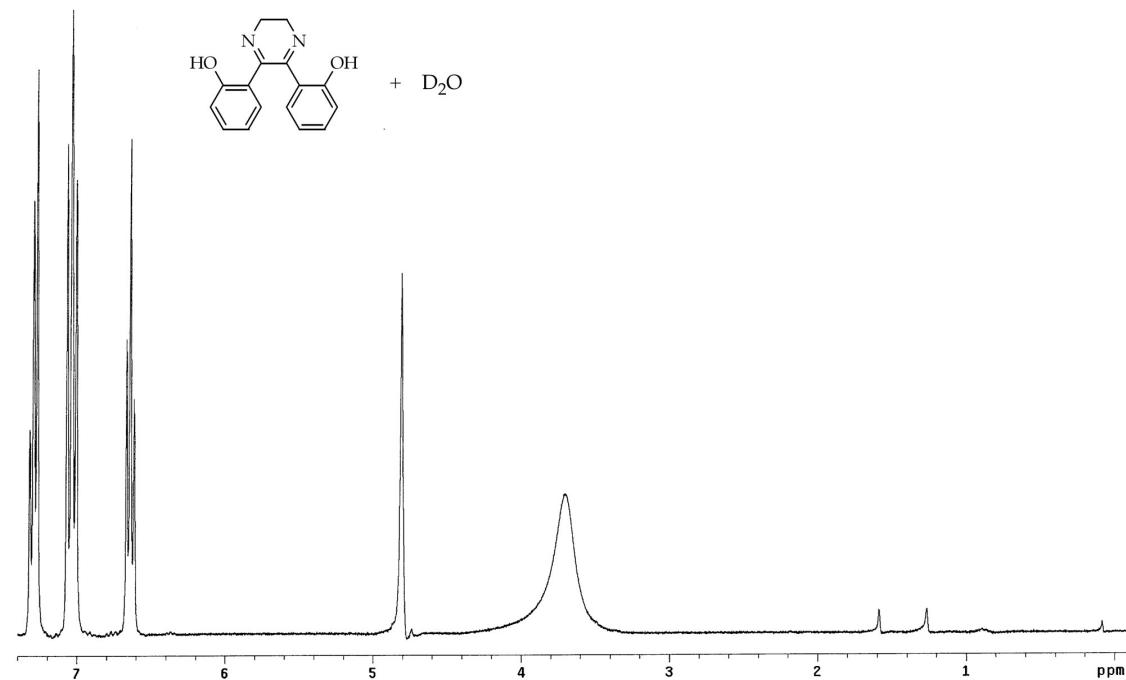
**NMR Analysis of Turnover Numbers.** General Procedure: In a 250 mL round bottom flask, 10.0 mmol of the desired substrate and 4.0 mmol of NaCN (0.196g, **40 mol%**) were dissolved in 50 mL of *N,N*-dimethylformamide. The reactions were then allowed to stir at room temperature. At the specified times, 2 mL aliquots were removed and placed into a separate flask; solvent was removed by rotary evaporation and high vacuum before the addition of CDCl<sub>3</sub> and <sup>1</sup>H NMR analysis.

<sup>1</sup>H NMR Spectra

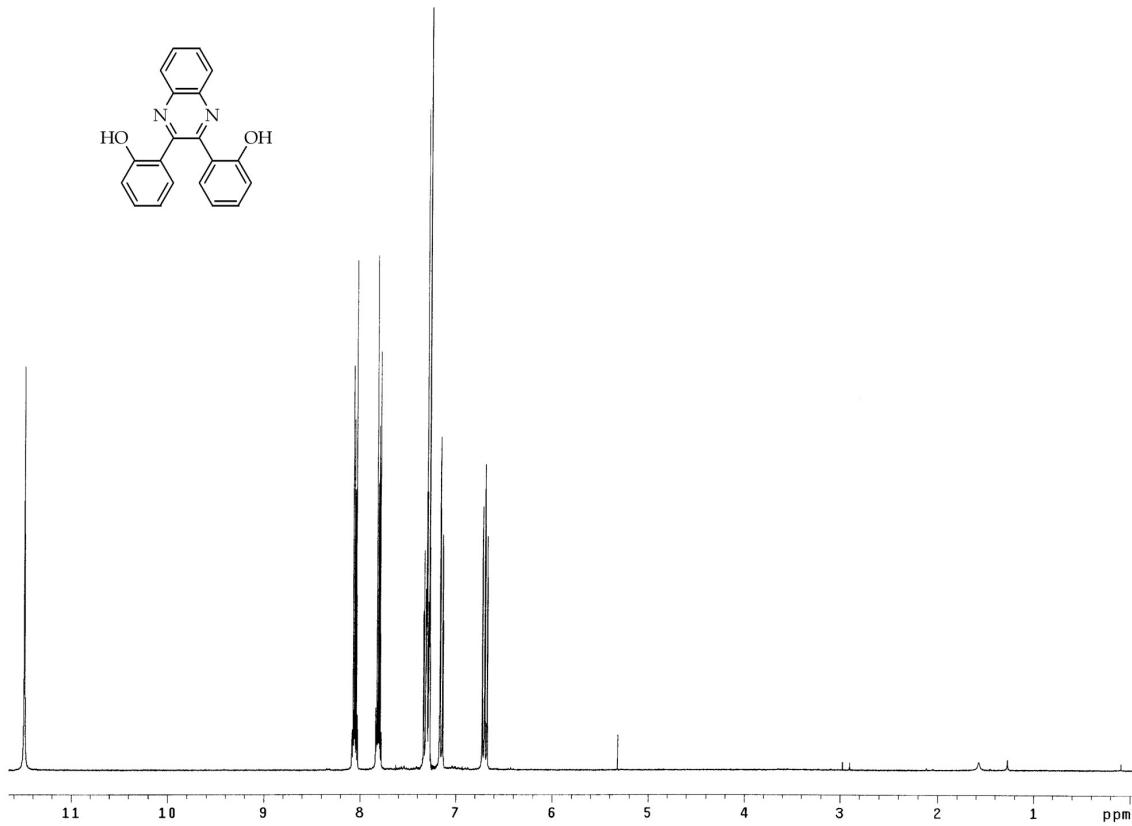
5,6-di-(2-hydroxyphenyl)-2,3-dihydropyrazine



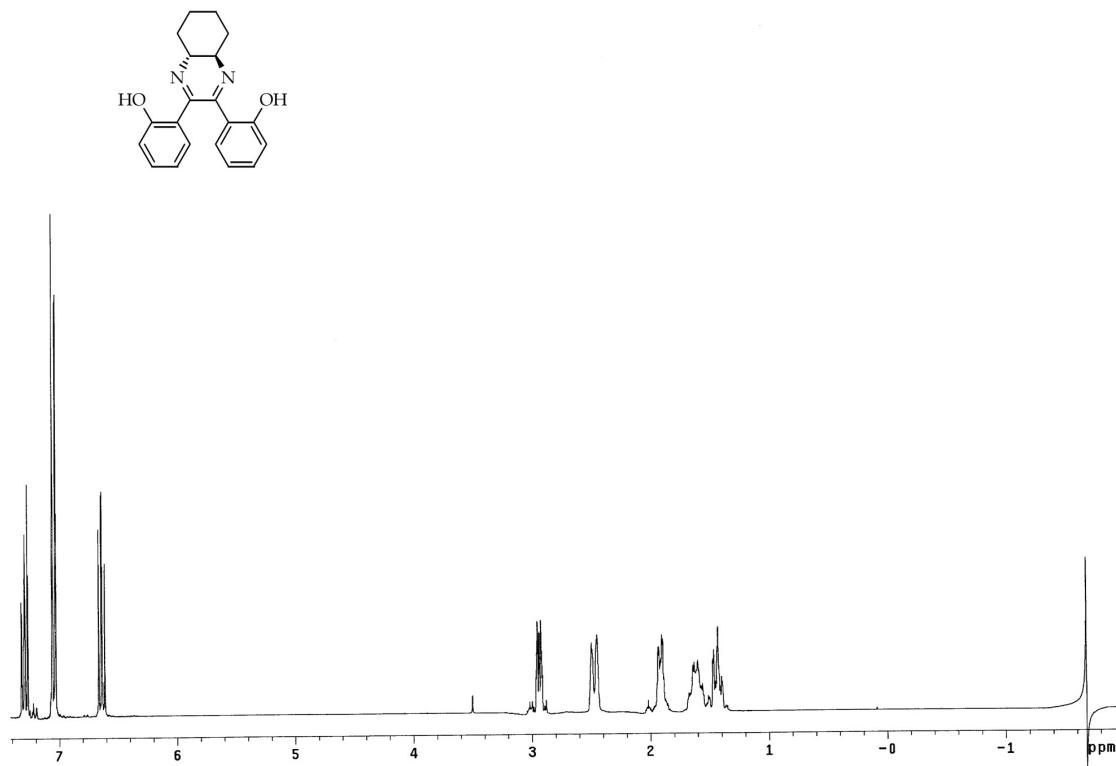
5,6-di-(2-hydroxyphenyl)-2,3-dihydropyrazine plus D<sub>2</sub>O



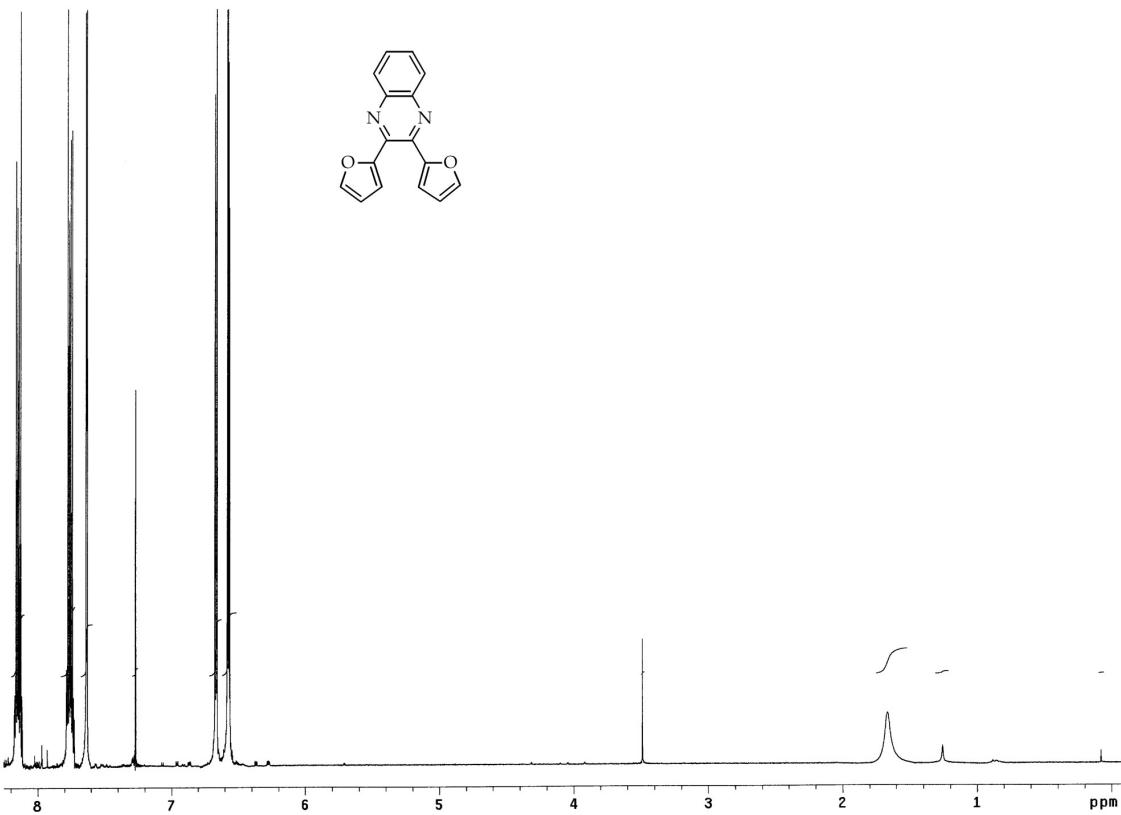
**2,3-di-(2-hydroxyphenyl)-quinoxaline.**



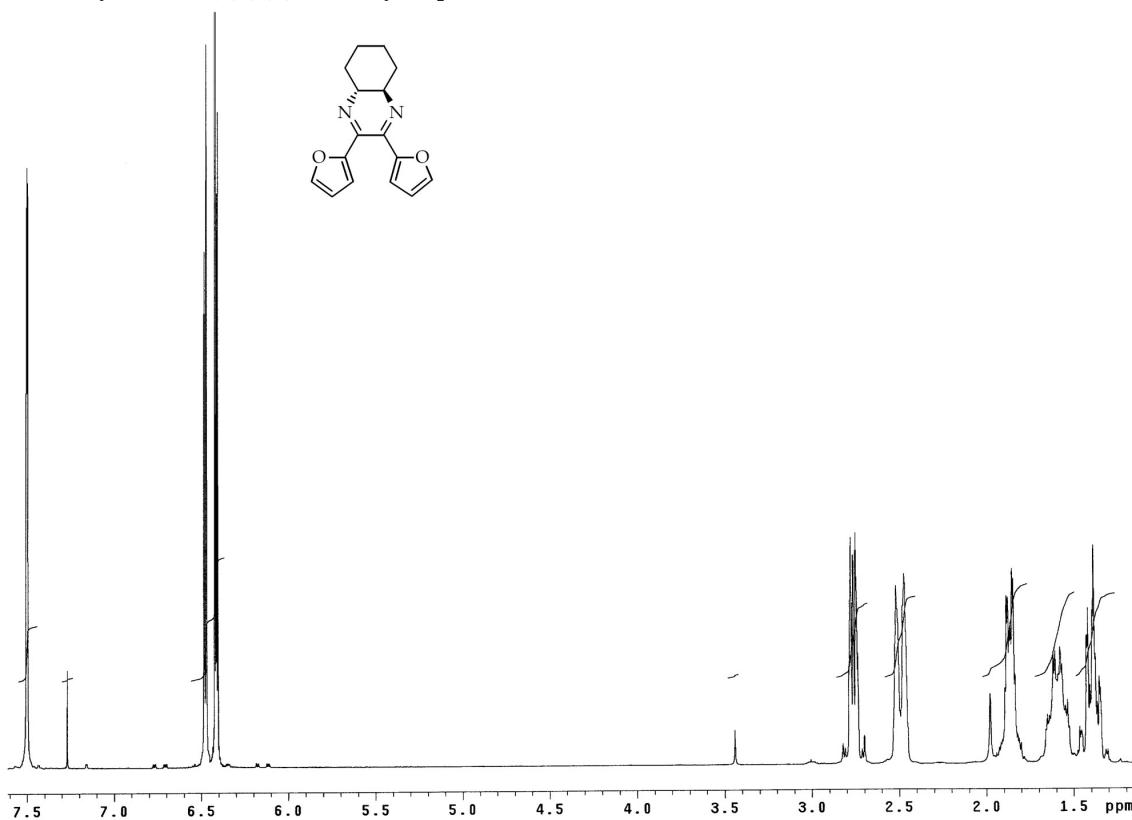
**(+/-)-2,3-di-(2-hydroxyphenyl)-*trans*-4a,5,6,7,8,8a-hexahydroquinoxaline.**



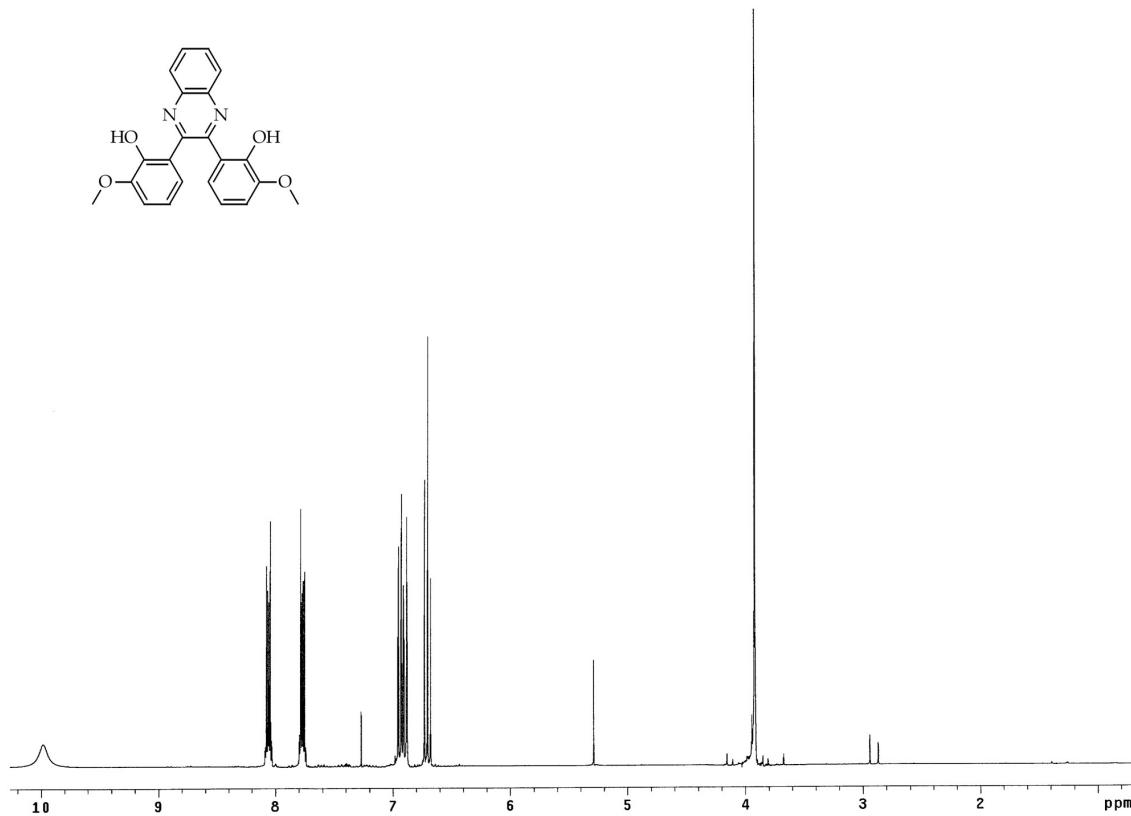
**2,3-di-(2-furyl)-quinoxaline.**



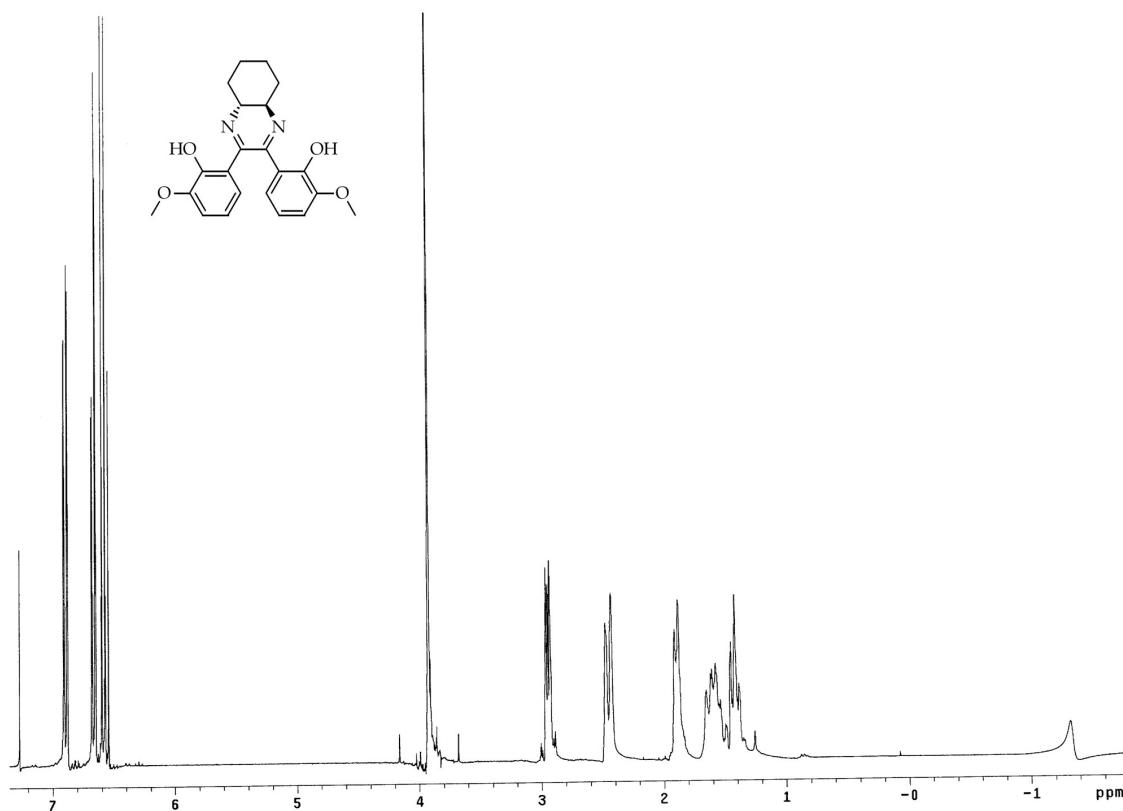
**(+/-)-2,3-di-(2-furyl)-*trans*-4a,5,6,7,8,8a-hexahydroquinoxaline.**



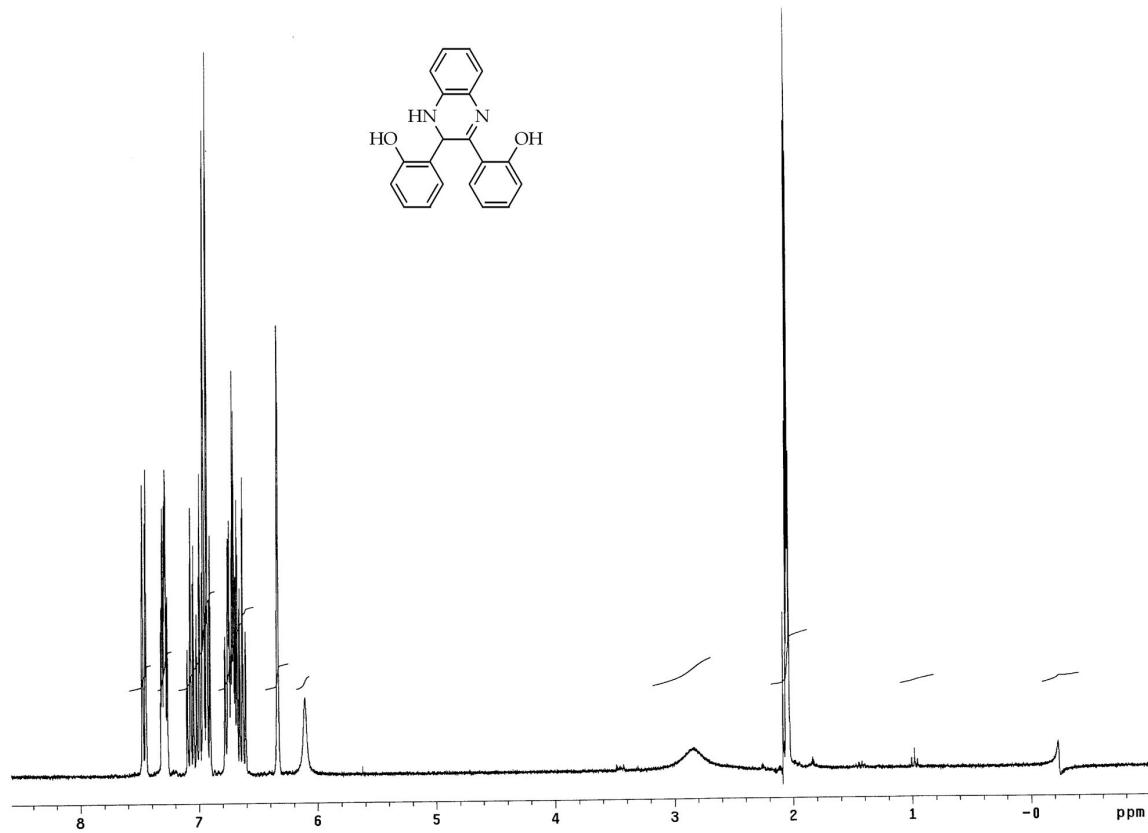
**2,3-di-(2-hydroxy-3-methoxy-phenyl)-quinoxaline.**



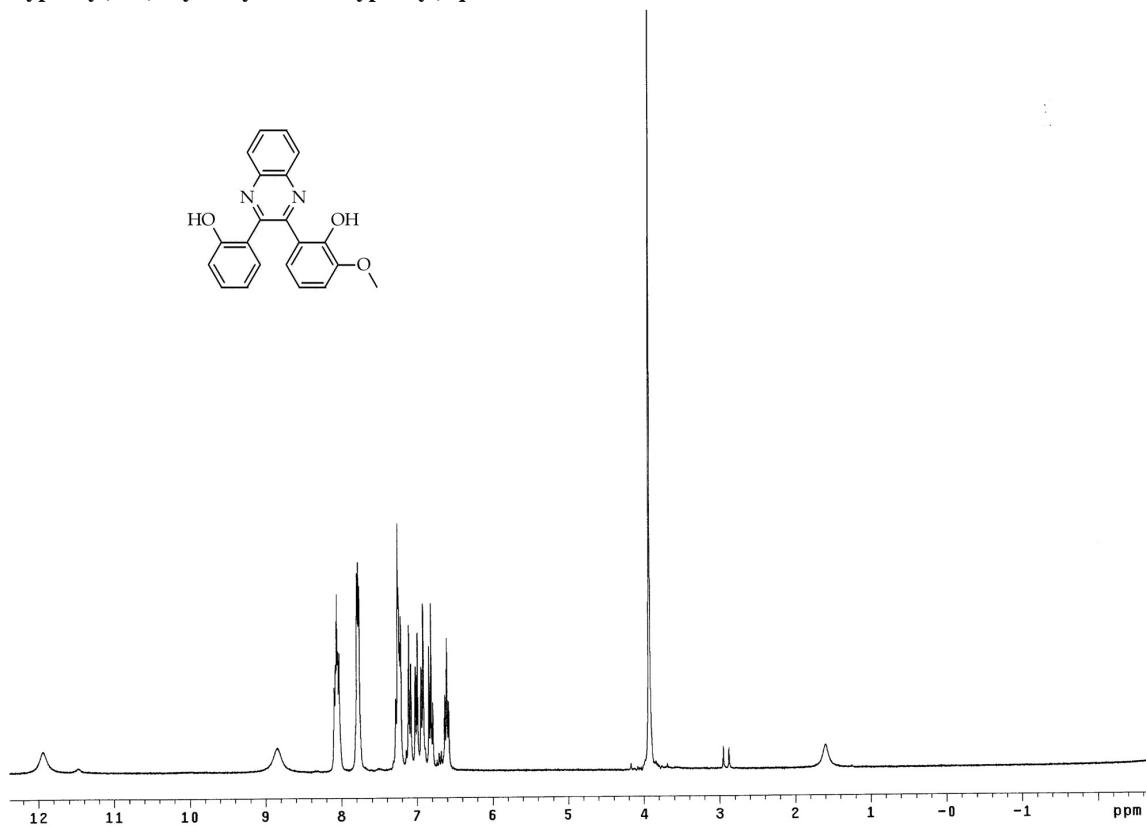
**(+/-)-2,3-di-(2-hydroxy-3-methoxy-phenyl)-*trans*-4a,5,6,7,8,8a-hexahydroquinoxaline.**



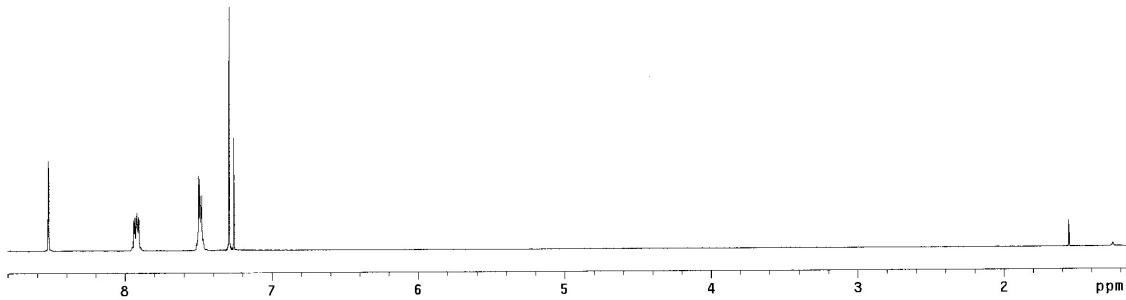
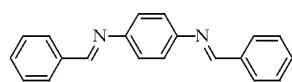
(+/-)-2,3-di-(2-hydroxyphenyl)-1,2-dihydroquinoxaline.



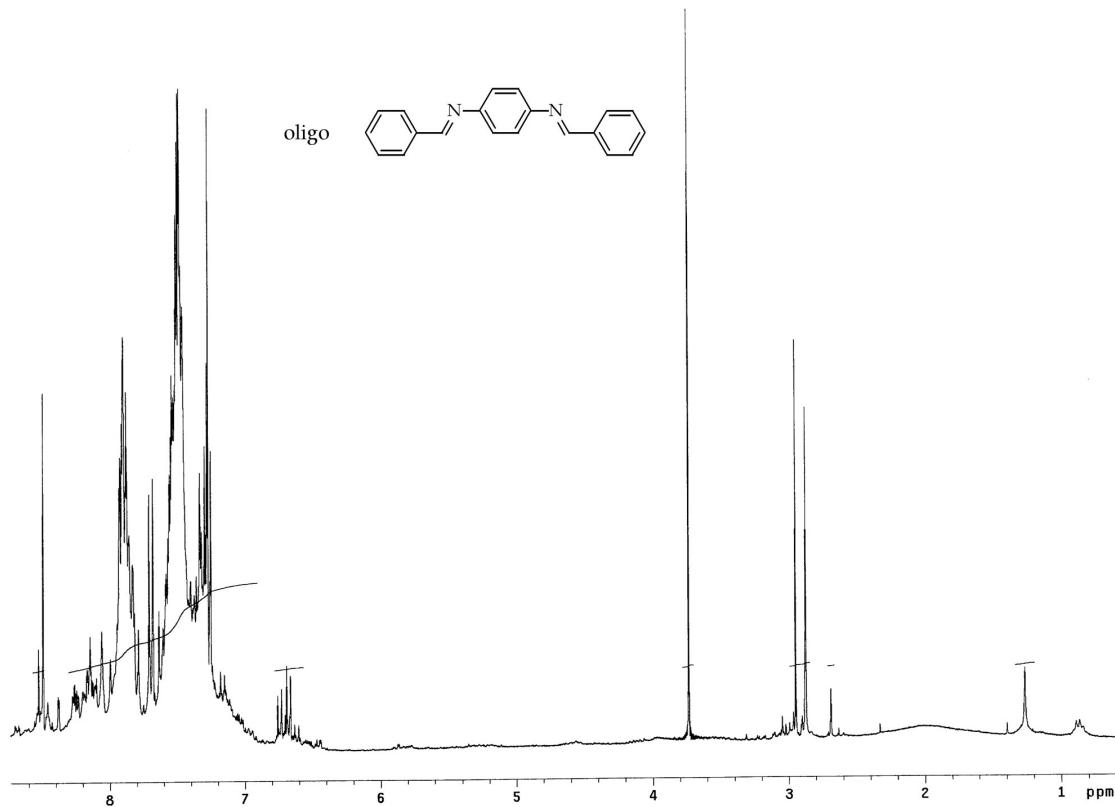
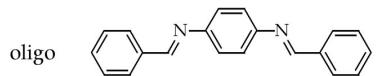
2-(2-hydroxyphenyl)-3-(2-hydroxy-3-methoxyphenyl)-quinoxaline.



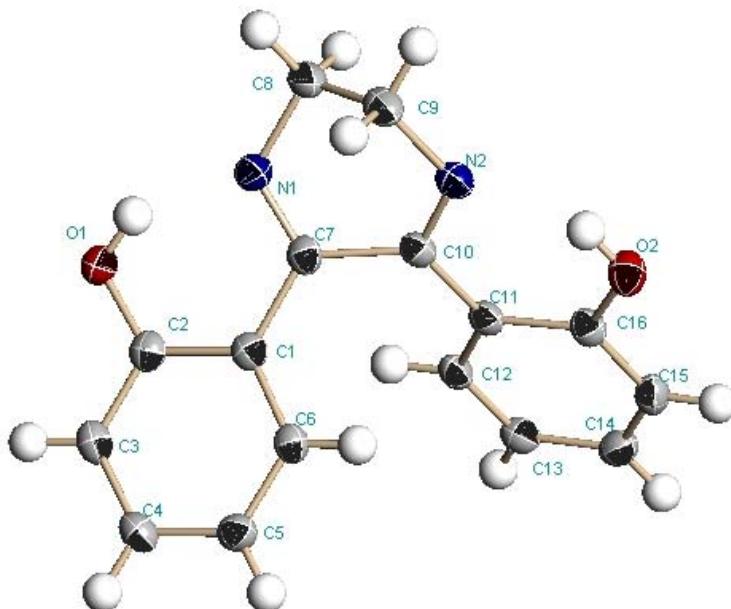
***N,N'*-bis(benzylidene)-*p*-phenylenediamine**



**oligo-[*N,N'*-bis(benzylidene)-*p*-phenylenediamine]**



# X-Ray Structure Data for 5,6-di-(2-hydroxyphenyl)-2,3-dihydropyrazine (SM08)



Labeled view with 50% probability ellipsoids

**Table 1.** Crystal structure and data refinement for data for 5,6-di-(2-hydroxyphenyl)-2,3-dihydro-pyrazine (SM08):  $C_{16}H_{14}N_2O_2$

Identification code	SM08
Empirical formula	$C_{16}H_{14}N_2O_2$
Formula weight	266.29
Temperature	110(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1 (No. 2)
Unit cell dimensions	$a = 5.8600(7)$ Å $\alpha = 101.721(2)^\circ$ . $b = 8.4944(10)$ Å $\beta = 98.011(2)^\circ$ . $c = 13.4511(17)$ Å $\gamma = 99.562(2)^\circ$ .
Volume	636.01(13) Å <sup>3</sup>
Z	2
Density (calculated)	1.391 Mg/m <sup>3</sup>
Absorption coefficient	0.093 mm <sup>-1</sup>
F(000)	280
Crystal size	0.3 × 0.3 × 0.1 mm <sup>3</sup>
Theta range for data collection	1.57 to 24.99°.
Index ranges	-6<=h<=6, -10<=k<=9, -15<=l<=11
Reflections collected	3280
Independent reflections	2189 [R(int) = 0.0182]
Completeness to theta = 24.99°	98.3 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2189 / 0 / 184
Goodness-of-fit on F <sup>2</sup>	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0602, wR2 = 0.1569
R indices (all data)	R1 = 0.0648, wR2 = 0.1701
Extinction coefficient	0.038(12)
Largest diff. peak and hole	0.506 and -0.382 e.Å <sup>-3</sup>

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for SM08. U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}^T$  tensor.

	x	y	z	U(eq)
O(1)	316(2)	10768(1)	1369(1)	32(1)
O(2)	10051(2)	6674(2)	2255(1)	33(1)
N(1)	2615(2)	8573(2)	698(1)	29(1)
N(2)	6623(2)	7158(2)	982(1)	28(1)
C(1)	4282(3)	10737(2)	2161(1)	25(1)
C(2)	2328(3)	11508(2)	2042(1)	26(1)
C(3)	2455(3)	13092(2)	2617(1)	29(1)
C(4)	4500(3)	13937(2)	3284(1)	30(1)
C(5)	6461(3)	13215(2)	3384(1)	29(1)
C(6)	6344(3)	11641(2)	2832(1)	26(1)
C(7)	4206(3)	9099(2)	1517(1)	26(1)
C(8)	2840(3)	7096(2)	-32(1)	34(1)
C(9)	5417(3)	7143(2)	-53(1)	32(1)
C(10)	5980(3)	8049(2)	1745(1)	25(1)
C(11)	6900(3)	7966(2)	2803(1)	24(1)
C(12)	5752(3)	8456(2)	3625(1)	25(1)
C(13)	6600(3)	8366(2)	4617(1)	28(1)
C(14)	8675(3)	7788(2)	4812(1)	30(1)
C(15)	9818(3)	7258(2)	4020(1)	29(1)
C(16)	8925(3)	7295(2)	3010(1)	26(1)

**Table 3.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for 5,6-di-(2-hydroxyphenyl)-2,3-dihydro-pyrazine (SM08):  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$ .

O(1)-C(2)	1.352(2)
O(2)-C(16)	1.3535(19)
N(1)-C(7)	1.288(2)
N(1)-C(8)	1.465(2)
N(2)-C(10)	1.286(2)
N(2)-C(9)	1.468(2)
C(1)-C(6)	1.404(2)
C(1)-C(2)	1.417(2)
C(1)-C(7)	1.472(2)
C(2)-C(3)	1.393(2)
C(3)-C(4)	1.382(2)
C(4)-C(5)	1.393(2)
C(5)-C(6)	1.377(2)
C(7)-C(10)	1.517(2)
C(8)-C(9)	1.508(3)
C(10)-C(11)	1.470(2)
C(11)-C(12)	1.400(2)
C(11)-C(16)	1.417(2)
C(12)-C(13)	1.379(2)
C(13)-C(14)	1.397(2)
C(14)-C(15)	1.375(2)
C(15)-C(16)	1.395(2)
C(7)-N(1)-C(8)	117.09(13)
C(10)-N(2)-C(9)	116.38(13)
C(6)-C(1)-C(2)	118.05(15)
C(6)-C(1)-C(7)	121.40(14)
C(2)-C(1)-C(7)	120.26(14)
O(1)-C(2)-C(3)	117.83(14)
O(1)-C(2)-C(1)	122.20(14)
C(3)-C(2)-C(1)	119.96(15)
C(4)-C(3)-C(2)	120.46(15)
C(3)-C(4)-C(5)	120.22(15)
C(6)-C(5)-C(4)	119.83(15)
C(5)-C(6)-C(1)	121.41(14)
N(1)-C(7)-C(1)	118.00(14)
N(1)-C(7)-C(10)	118.79(14)
C(1)-C(7)-C(10)	123.14(13)
N(1)-C(8)-C(9)	108.42(14)
N(2)-C(9)-C(8)	108.98(13)
N(2)-C(10)-C(11)	119.29(13)

N(2)-C(10)-C(7)	118.58(14)
C(11)-C(10)-C(7)	122.08(13)
C(12)-C(11)-C(16)	117.82(14)
C(12)-C(11)-C(10)	121.70(13)
C(16)-C(11)-C(10)	120.39(14)
C(13)-C(12)-C(11)	121.83(14)
C(12)-C(13)-C(14)	119.25(15)
C(15)-C(14)-C(13)	120.52(15)
C(14)-C(15)-C(16)	120.42(14)
O(2)-C(16)-C(15)	117.80(14)
O(2)-C(16)-C(11)	122.22(14)
C(15)-C(16)-C(11)	119.99(14)

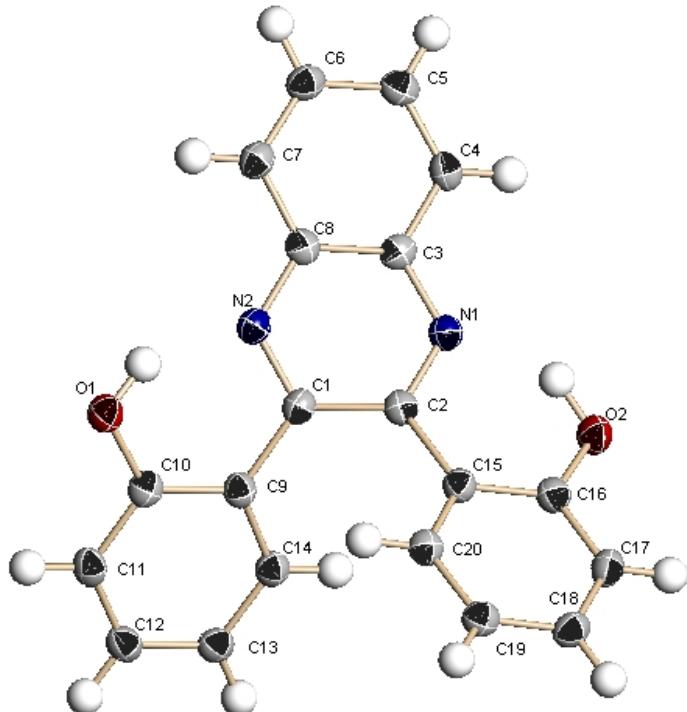
**Table 4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for SM08. The anisotropic displacement factor exponent takes the form:  $-2p^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
O(1)	29(1)	32(1)	33(1)	4(1)	0(1)	9(1)
O(2)	33(1)	40(1)	33(1)	11(1)	10(1)	15(1)
N(1)	34(1)	27(1)	26(1)	5(1)	1(1)	6(1)
N(2)	32(1)	24(1)	27(1)	6(1)	7(1)	6(1)
C(1)	28(1)	25(1)	23(1)	9(1)	7(1)	6(1)
C(2)	28(1)	30(1)	25(1)	11(1)	7(1)	7(1)
C(3)	31(1)	29(1)	32(1)	11(1)	11(1)	11(1)
C(4)	37(1)	24(1)	32(1)	7(1)	11(1)	9(1)
C(5)	31(1)	26(1)	30(1)	6(1)	3(1)	3(1)
C(6)	28(1)	26(1)	28(1)	10(1)	7(1)	7(1)
C(7)	28(1)	26(1)	25(1)	9(1)	6(1)	7(1)
C(8)	42(1)	28(1)	28(1)	3(1)	-2(1)	10(1)
C(9)	46(1)	29(1)	23(1)	7(1)	7(1)	11(1)
C(10)	26(1)	20(1)	27(1)	5(1)	6(1)	3(1)
C(11)	26(1)	19(1)	27(1)	5(1)	5(1)	4(1)
C(12)	26(1)	19(1)	29(1)	5(1)	4(1)	4(1)
C(13)	33(1)	24(1)	26(1)	4(1)	6(1)	5(1)
C(14)	32(1)	27(1)	28(1)	7(1)	-1(1)	2(1)
C(15)	25(1)	26(1)	35(1)	10(1)	3(1)	5(1)
C(16)	26(1)	23(1)	31(1)	7(1)	7(1)	5(10)

**Table 5.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for SM08.

H(1)	534	9919	981	48
H(2)	9248	6621	1677	50
H(3)	1126	13593	2551	35
H(4)	4569	15015	3675	36
H(5)	7875	13807	3832	35
H(6)	7688	11156	2907	31
H(8A)	1993	7060	-730	40
H(8B)	2147	6104	184	40
H(9A)	5611	6170	-556	38
H(9B)	6108	8139	-268	38
H(12)	4349	8861	3495	30
H(13)	5782	8695	5161	34
H(14)	9301	7760	5497	36
H(15)	11225	6863	4162	34

## X-Ray Structure Data for 2,3-di-(2-hydroxyphenyl)-quinoxaline (SM12)



### Labeled view with 50% probability ellipsoids

**Table 1.** Crystal data and structure refinement for 2,3-di-(2-hydroxyphenyl)quinoxaline (SM12):  $C_{20}H_{14}N_2O_2$ .

Identification code	SM12
Empirical formula	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	314.33
Temperature	110(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 5.9430(9) Å b = 8.6856(13) Å c = 14.988(2) Å 733.64(19) Å <sup>3</sup> 2
Volume	
Z	
Density (calculated)	1.423 Mg/m <sup>3</sup>
Absorption coefficient	0.093 mm <sup>-1</sup>
F(000)	328
Crystal size	0.4 x 0.2 x 0.07 mm <sup>3</sup>
Theta range for data collection	2.44 to 25.00°.
Index ranges	-7<=h<=7, -10<=k<=10, -17<=l<=17
Reflections collected	9322
Independent reflections	2472 [R(int) = 0.0229]
Completeness to theta = 25.00°	96.1 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2472 / 0 / 225
Goodness-of-fit on F <sup>2</sup>	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0572, wR2 = 0.1430
R indices (all data)	R1 = 0.0625, wR2 = 0.1515
Largest diff. peak and hole	0.581 and -0.291 e.Å <sup>-3</sup>

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 2,3-di-(2-hydroxyphenyl)quinoxaline (SM12):  $C_{20}H_{14}N_2O_2$ . U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
O(1)	14115(2)	9087(1)	1776(1)	33(1)
O(2)	4079(2)	4771(1)	2350(1)	34(1)
N(1)	7517(2)	6157(2)	1227(1)	27(1)
N(2)	11134(2)	8059(2)	972(1)	27(1)
C(1)	9961(2)	7559(2)	1812(1)	25(1)
C(2)	8295(2)	6379(2)	1960(1)	25(1)
C(3)	8569(3)	6807(2)	347(1)	27(1)
C(4)	7795(3)	6539(2)	-439(1)	29(1)
C(5)	9048(3)	7020(2)	-1302(1)	31(1)
C(6)	11080(3)	7788(2)	-1413(1)	31(1)
C(7)	11812(3)	8121(2)	-668(1)	29(1)
C(8)	10537(3)	7649(2)	226(1)	27(1)
C(9)	10307(3)	8377(2)	2522(1)	26(1)
C(10)	12327(3)	9137(2)	2455(1)	28(1)
C(11)	12532(3)	10000(2)	3097(1)	30(1)
C(12)	10724(3)	10188(2)	3767(1)	31(1)
C(13)	8685(3)	9498(2)	3821(1)	29(1)
C(14)	8493(3)	8602(2)	3206(1)	28(1)
C(15)	7486(3)	5317(2)	2885(1)	27(1)
C(16)	5433(3)	4557(2)	3033(1)	28(1)
C(17)	4731(3)	3546(2)	3901(1)	30(1)
C(18)	6067(3)	3226(2)	4619(1)	31(1)
C(19)	8142(3)	3901(2)	4471(1)	30(1)
C(20)	8842(3)	4931(2)	3614(1)	28(1)

**Table 3.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for 2,3-di-(2-hydroxyphenyl)quinoxaline (SM12).

O(1)-C(10)	1.3579(19)
O(2)-C(16)	1.3605(19)
N(1)-C(2)	1.3236(19)
N(1)-C(3)	1.366(2)
N(2)-C(1)	1.325(2)
N(2)-C(8)	1.368(2)
C(1)-C(2)	1.454(2)
C(1)-C(9)	1.480(2)
C(2)-C(15)	1.484(2)
C(3)-C(8)	1.410(2)
C(3)-C(4)	1.412(2)
C(4)-C(5)	1.370(2)
C(5)-C(6)	1.410(2)
C(6)-C(7)	1.368(2)
C(7)-C(8)	1.412(2)
C(9)-C(14)	1.403(2)
C(9)-C(10)	1.411(2)
C(10)-C(11)	1.397(2)
C(11)-C(12)	1.380(2)
C(12)-C(13)	1.393(2)
C(13)-C(14)	1.383(2)
C(15)-C(20)	1.404(2)
C(15)-C(16)	1.411(2)
C(16)-C(17)	1.389(2)
C(17)-C(18)	1.386(2)
C(18)-C(19)	1.385(2)
C(19)-C(20)	1.384(2)
C(2)-N(1)-C(3)	119.78(13)
C(1)-N(2)-C(8)	119.73(13)
N(2)-C(1)-C(2)	119.50(13)
N(2)-C(1)-C(9)	116.16(13)
C(2)-C(1)-C(9)	124.09(13)
N(1)-C(2)-C(1)	118.95(14)
N(1)-C(2)-C(15)	116.68(13)
C(1)-C(2)-C(15)	124.27(13)
N(1)-C(3)-C(8)	119.89(14)

N(1)-C(3)-C(4)	120.27(14)
C(8)-C(3)-C(4)	119.68(14)
C(5)-C(4)-C(3)	119.33(14)
C(4)-C(5)-C(6)	120.76(14)
C(7)-C(6)-C(5)	120.96(14)
C(6)-C(7)-C(8)	119.21(15)
N(2)-C(8)-C(3)	119.36(14)
N(2)-C(8)-C(7)	120.68(14)
C(3)-C(8)-C(7)	119.90(14)
C(14)-C(9)-C(10)	118.13(14)
C(14)-C(9)-C(1)	119.94(13)
C(10)-C(9)-C(1)	121.34(14)
O(1)-C(10)-C(11)	117.41(14)
O(1)-C(10)-C(9)	122.65(14)
C(11)-C(10)-C(9)	119.94(14)
C(12)-C(11)-C(10)	120.45(14)
C(11)-C(12)-C(13)	120.38(14)
C(14)-C(13)-C(12)	119.48(15)
C(13)-C(14)-C(9)	121.50(14)
C(20)-C(15)-C(16)	117.96(14)
C(20)-C(15)-C(2)	120.76(14)
C(16)-C(15)-C(2)	121.06(14)
O(2)-C(16)-C(17)	117.62(14)
O(2)-C(16)-C(15)	122.37(14)
C(17)-C(16)-C(15)	120.01(15)
C(18)-C(17)-C(16)	120.77(15)
C(19)-C(18)-C(17)	119.93(14)
C(20)-C(19)-C(18)	119.82(14)
C(19)-C(20)-C(15)	121.37(15)

**Table 4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 2,3-di-(2-hydroxyphenyl)quinoxaline (SM12):  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2$ . The anisotropic displacement factor exponent takes the form:  $-2p^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
O(1)	27(1)	36(1)	37(1)	-14(1)	0(1)	-5(1)
O(2)	31(1)	40(1)	33(1)	-6(1)	-7(1)	-9(1)
N(1)	25(1)	27(1)	29(1)	-7(1)	-4(1)	-1(1)
N(2)	28(1)	25(1)	28(1)	-5(1)	-3(1)	-2(1)
C(1)	22(1)	23(1)	28(1)	-4(1)	-2(1)	-1(1)
C(2)	22(1)	24(1)	29(1)	-7(1)	-4(1)	1(1)
C(3)	27(1)	23(1)	28(1)	-4(1)	-4(1)	2(1)
C(4)	29(1)	25(1)	34(1)	-7(1)	-7(1)	-3(1)
C(5)	37(1)	26(1)	28(1)	-6(1)	-8(1)	1(1)
C(6)	36(1)	26(1)	27(1)	-3(1)	-1(1)	-1(1)
C(7)	30(1)	25(1)	30(1)	-4(1)	-2(1)	-3(1)
C(8)	28(1)	22(1)	30(1)	-6(1)	-6(1)	1(1)
C(9)	28(1)	22(1)	27(1)	-3(1)	-6(1)	-3(1)
C(10)	27(1)	25(1)	29(1)	-3(1)	-4(1)	-1(1)
C(11)	31(1)	28(1)	31(1)	-3(1)	-11(1)	-5(1)
C(12)	39(1)	26(1)	28(1)	-6(1)	-9(1)	-4(1)
C(13)	34(1)	27(1)	25(1)	-4(1)	-4(1)	-3(1)
C(14)	29(1)	27(1)	26(1)	-3(1)	-5(1)	-3(1)
C(15)	27(1)	27(1)	29(1)	-9(1)	-1(1)	-4(1)
C(16)	28(1)	27(1)	29(1)	-8(1)	-4(1)	-2(1)
C(17)	28(1)	27(1)	34(1)	-7(1)	0(1)	-6(1)
C(18)	36(1)	26(1)	28(1)	-3(1)	1(1)	-3(1)
C(19)	32(1)	28(1)	28(1)	-6(1)	-6(1)	0(1)
C(20)	28(1)	25(1)	31(1)	-8(1)	-4(1)	-1(1)

**Table 5.** Hydrogen coordinates ( $x \times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 2,3-di-(2-hydroxyphenyl)quinoxaline (SM12):  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2$ .

	$x$	$y$	$z$	$U(\text{eq})$
H(1O1)	13560(30)	8780(30)	1316(15)	48(6)
H(1O2)	4900(40)	5260(30)	1748(16)	59(6)

H(4A)	6420	6031	-371	35
H(5A)	8541	6835	-1832	37
H(6A)	11954	8078	-2013	37
H(7A)	13163	8664	-752	35
H(11A)	13925	10459	3073	36
H(12A)	10872	10792	4194	37
H(13A)	7435	9642	4278	35
H(14A)	7102	8129	3247	33
H(17A)	3319	3069	4003	36
H(18A)	5560	2544	5212	37
H(19A)	9082	3658	4957	36
H(20A)	10270	5386	3518	33

**Table 6.** Torsion angles [°] for 2,3-di-(2-hydroxyphenyl)quinoxaline (SM12): C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>.

C(8)-N(2)-C(1)-C(2)	9.7(2)
C(8)-N(2)-C(1)-C(9)	-164.78(13)
C(3)-N(1)-C(2)-C(1)	11.8(2)
C(3)-N(1)-C(2)-C(15)	-164.65(13)
N(2)-C(1)-C(2)-N(1)	-18.6(2)
C(9)-C(1)-C(2)-N(1)	155.39(14)
N(2)-C(1)-C(2)-C(15)	157.55(14)
C(9)-C(1)-C(2)-C(15)	-28.4(2)
C(2)-N(1)-C(3)-C(8)	2.8(2)
C(2)-N(1)-C(3)-C(4)	178.18(14)
N(1)-C(3)-C(4)-C(5)	-171.50(14)
C(8)-C(3)-C(4)-C(5)	3.8(2)
C(3)-C(4)-C(5)-C(6)	-0.5(2)
C(4)-C(5)-C(6)-C(7)	-2.3(2)
C(5)-C(6)-C(7)-C(8)	1.7(2)
C(1)-N(2)-C(8)-C(3)	5.0(2)
C(1)-N(2)-C(8)-C(7)	-177.78(14)
N(1)-C(3)-C(8)-N(2)	-11.8(2)
C(4)-C(3)-C(8)-N(2)	172.82(14)
N(1)-C(3)-C(8)-C(7)	170.93(14)
C(4)-C(3)-C(8)-C(7)	-4.4(2)
C(6)-C(7)-C(8)-N(2)	-175.53(14)
C(6)-C(7)-C(8)-C(3)	1.7(2)
N(2)-C(1)-C(9)-C(14)	146.65(14)
C(2)-C(1)-C(9)-C(14)	-27.6(2)
N(2)-C(1)-C(9)-C(10)	-24.5(2)
C(2)-C(1)-C(9)-C(10)	161.33(14)
C(14)-C(9)-C(10)-O(1)	-175.23(13)
C(1)-C(9)-C(10)-O(1)	-4.0(2)
C(14)-C(9)-C(10)-C(11)	4.0(2)
C(1)-C(9)-C(10)-C(11)	175.24(14)
O(1)-C(10)-C(11)-C(12)	175.73(13)
C(9)-C(10)-C(11)-C(12)	-3.5(2)
C(10)-C(11)-C(12)-C(13)	1.1(2)
C(11)-C(12)-C(13)-C(14)	0.9(2)
C(12)-C(13)-C(14)-C(9)	-0.3(2)
C(10)-C(9)-C(14)-C(13)	-2.1(2)
C(1)-C(9)-C(14)-C(13)	-173.48(14)
N(1)-C(2)-C(15)-C(20)	151.67(15)
C(1)-C(2)-C(15)-C(20)	-24.6(2)
N(1)-C(2)-C(15)-C(16)	-22.8(2)
C(1)-C(2)-C(15)-C(16)	160.92(14)
C(20)-C(15)-C(16)-O(2)	-175.59(14)
C(2)-C(15)-C(16)-O(2)	-1.0(2)
C(20)-C(15)-C(16)-C(17)	4.2(2)
C(2)-C(15)-C(16)-C(17)	178.88(14)
O(2)-C(16)-C(17)-C(18)	177.57(14)
C(15)-C(16)-C(17)-C(18)	-2.3(2)
C(16)-C(17)-C(18)-C(19)	-0.8(2)
C(17)-C(18)-C(19)-C(20)	1.9(2)
C(18)-C(19)-C(20)-C(15)	0.2(2)
C(16)-C(15)-C(20)-C(19)	-3.3(2)
C(2)-C(15)-C(20)-C(19)	-177.91(14)