Highly Stable Keto-Enamine Salicylideneanilines

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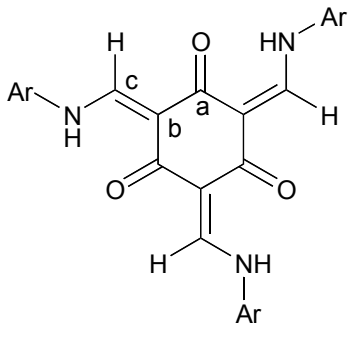
Supporting Information

Materials and Equipment. Ethanol was distilled from Mg prior to use. BOC-protected phenylenediamine **5d** was prepared by a literature procedure.[1] All other chemicals were purchased from Aldrich or Fisher and used as received. ^{1}H NMR spectra (300 MHz) were recorded on a Bruker Avance 300 spectrometer and were referenced internally to residual $CHCl_3$ or $Cl_2CDCHCl_2$. ^{13}C NMR spectra (75.4 or 100.6 MHz) were recorded on Bruker Avance 300 or Bruker Avance 400 spectrometers and were referenced internally to $CDCl_3$ or $Cl_2CDCHCl_2$. High temperature VT NMR spectra were obtained on a Bruker Avance 300 spectrometer and were referenced internally to residual $Cl_2CDCHCl_2$. ^{1}H COSY spectra were obtained on a Bruker Avance 300 spectrometer and were referenced internally to residual $Cl_2CDCHCl_2$. UV-vis spectra were obtained in CH_2Cl_2 or $CHCl_3$ on a double-beam ATI Unicam UV2 spectrometer using a 1 cm quartz cuvette. IR spectra were obtained as KBr presses with a Bomem MB-Series spectrometer. Melting points were obtained on a Fisher-John's melting point apparatus and are uncorrected. Elemental analyses were obtained in the UBC EA Facility. Mass spectra were obtained in the UBC Mass Spectrometry Facility. Ab initio and semi-empirical caclulations were performed on a Pentium IV processor operating at 2.66 GHz with Spartan '02 for Windows.

Synthesis of triformylphloroglucinol (4). To hexamethylenetetraamine (15.098 g, 108 mmol) and dried phloroglucinol (6.014 g, 49 mmol) under N_2 was added 90 mL trifluoroacetic acid. The solution was heated at 100 ºC for *ca.* 2.5 h. Approximately 150 mL of 3 M HCl was added and the solution was heated at 100 ºC for 1 h. After cooling to room temperature, the solution was filtered through Celite, extracted with *ca.* 350 mL dichloromethane, dried over magnesium sulfate, and filtered. Rotary evaporation of the solution afforded 1.48 g (7.0 mmol, 14%) of an off-white powder. ^{1}H NMR indicated near 99% purity; a pure sample was obtained by sublimation.

Data for 4: ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.10 (s, 3H, OH), 10.14 (s, 3H, CHO) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 192.1 (*C*HO), 173.6 (*C*OH), 102.9 (*C*CHO) ppm; MS (EI, 70 eV) *m/z* 210 (M^+), 182, 153; IR ν (KBr) = 2950, 1641, 1604, 1433, 1390, 1253, 1193, 968, 876, 607 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} 270 nm ($\varepsilon = 4.90\times10^4$ L mol^{-1} cm^{-1}); TLC (silica gel, CH_2Cl_2) R_f ~ 0.3 (streaks); Mp. = 198-200 ºC; Anal. Calcd for $C_9H_6O_6$: C, 51.44; H, 2.88; N, 0.00. Found: C, 51.35; H, 2.79; N, < 0.05.

Below are shown the structures of the two geometric isomers present in compounds 6a-d for ^{13}C NMR data assignments. For each ^{13}C peak, the assignment is made to each carbon (letter) and each isomer (number), where possible to determine – for many of the peaks, the splitting could not be resolved. The ^{13}C NMR assignments were assisted with HMQC spectra.



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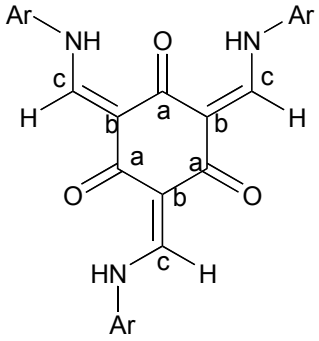

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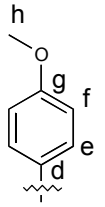
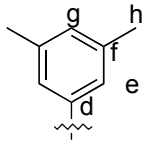
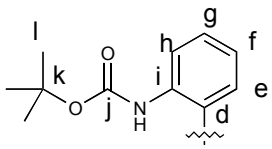


6b



6c



6d

Synthesis of 6a. To **4** (0.163 g, 0.8 mmol) in 50 mL ethanol was added aniline (0.500 g, 5.4 mmol) in 20 mL ethanol and the solution was heated to reflux for 1 d. The solution was cooled to room temperature and the precipitate was collected by filtration, washed with ethanol, and dried under vacuum to give 0.210 g (0.5 mmol, 62%) of a yellow solid. A ^{13}C NMR spectrum of **6a** could not be obtained due to poor solubility of the product.

Data for 6a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.0-13.4 (m, NH), 8.90 (d, HC-N), 8.77 (d, CH), 8.75 (d, CH), 7.44-7.17 (m, Ph) ppm; MS (EI, 70 eV) *m/z* 435 (M^+), 358, 343; IR ν (KBr) = 3443, 1616, 1635, 1581, 1553, 1465, 1444, 1340, 1287, 1236, 1041 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} 396 nm ($\varepsilon = 6.76\times10^4$ L mol^{-1} cm^{-1}); Mp. > 300 ºC; Anal. Calc'd for $C_{27}H_{21}N_3O_6$: C, 74.47; H, 4.86; N, 9.65. Found: C, 73.09; H, 4.81; N, 9.98.[2] HRMS-EI (M^+) Calc'd for $C_{27}H_{21}N_3O_3$ 435.15829, found 435.15825.

Synthesis of 6b. To **4** (0.137 g, 0.6 mmol) in 50 mL ethanol was added 4-methoxyaniline (0.383 g, 3.1 mmol) in 20 mL ethanol and the solution was heated to reflux overnight. The solution was cooled to room temperature and the precipitate was collected by filtration, washed with ethanol, and dried under vacuum to give 0.161 g (0.3 mmol, 52%) of a yellow solid.

Data for 6b: ^{1}H NMR (300 MHz, d^2-1,1,2,2-tetrachloroethane) δ 13.30 (d, J=13 Hz, =CNH), 13.20 (d, J=13 Hz, =CNH), 12.95 (d, J=13 Hz, =CNH), 8.67 (d, J=13 Hz, HC-N), 8.66 (d, J=13 Hz, HC-N), 8.60 (d, J=13 Hz, HC-N), 8.57 (d, J=13 Hz, HC-N), 7.19 (m, Ph), 6.89 (d, J=8 Hz, Ph), 3.79 (s, 9H, OCH_3) ppm; ^{13}C NMR (75.4 MHz, d^2-1,1,2,2-tetrachloroethane) δ 187.9 (C_{8a}), 185.30 (C_{7a}), 185.27 (C_{8a}), 182.4 (C_{8a}), 157.8 (C_g), 157.7 (C_g), 150.3 (C_{8c}), 149.7 (C_{8c}), 149.6 (C_{7c}), 148.7 (C_{8c}), 132.7 (C_d), 132.6 (C_d), 119.5 (C_f), 119.3 (C_f), 119.2 (C_f), 115.31 (C_e), 115.29(C_e), 106.54 (C_{8b}), 106.46 (C_{8b}), 106.41 (C_{8b}), 106.39 (C_{7b}), 55.9 (C_h) ppm; MS (EI, 70 eV) *m/z* 525 (M^+); IR ν (KBr) = 3436, 2833, 1617, 1607, 1555, 1515, 1456, 1422, 1292, 1247, 1173, 1113, 1084, 1036, 993, 823 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} 408 nm ($\varepsilon = 6.54\times10^4$ L mol^{-1} cm^{-1}); Mp. = 129-131 ºC; HRMS-EI (M^+) Calc'd for $C_{30}H_{27}N_3O_6$ 525.1899, found 525.1900.

Synthesis of 6c. To **4** (0.137 g, 0.6 mmol) in 50 mL ethanol was added 3,5-dimethylaniline (0.420 g, 3.1 mmol) in 20 mL ethanol and the solution was refluxed overnight. The solution was cooled to room temperature and the precipitate was collected by filtration, washed with ethanol and dried under vacuum to give 0.193 g (0.4 mmol, 57%) of a yellow solid.

Data for 6c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.20 (m, =CNH), 12.79 (m, =CNH), 8.74-8.61 (m, HC-N), 6.86-6.70 (m, Ph), 2.31 (s, CH_3) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 187.8 (C_{7a}), 185.2 (C_{7a}, C_{8a}), 182.5 (C_{7a}), 149.4 (C_{8c}), 148.9 (C_{8c}), 148.6 (C_{7c}), 147.9 (C_{8c}), 139.51 (C_d), 139.48 (C_d), 139.45 (C_d), 139.38 (C_d), 138.81 (C_f), 138.78 (C_f), 127.07 (C_g), 127.00 (C_g), 126.96 (C_g), 106.66 (C_{8b}), 106.56 (C_{8b}), 106.45 (C_{7b}), 106.44 (C_{7b}), 21.24 (C_{8h}), 21.21 (C_{7h}, C_{8h}), 21.19 (C_{7h}) ppm; MS (EI, 70 eV) *m/z* 519 (M^+); IR ν (KBr) = 3436, 3019, 2918, 2857, 1621, 1584, 1551, 1474, 1448, 1379, 1328, 1271, 1242, 1155, 1097, 1044, 997, 955, 833 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} 400 nm ($\varepsilon = 5.82\times10^4$ L mol^{-1} cm^{-1}); Mp. > 300 ºC; Anal. Calc'd for $C_{33}H_{33}N_3O_3$: C, 76.28; H, 6.40; N, 8.09. Found: C, 74.13; H, 6.27; N, 8.17.[2] HRMS-EI (M^+) Calc'd for $C_{33}H_{33}N_3O_3$ 519.25219, found 519.25221.

Synthesis of 6d. To **4** (0.137 g, 0.6 mmol) in 50 mL ethanol was added *N*-(*tert*-butyloxycarbonyl)1,2-diaminobenzene (0.642 g, 3.1 mmol) in 20 mL ethanol and the solution was heated to reflux overnight. The solution was cooled to room temperature and the precipitate was collected by filtration, washed with ethanol and dried under vacuum to give 0.312 g (0.4 mmol, 67%) of a yellow solid. The product was purified by recrystallization from CH_2Cl_2 /hexanes.

Data for 6d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.84-12.52 (m, =CHN), 8.62-8.27 (m, HC-N), 7.82 (m, Ph), 7.23 (m, Ph), 6.70 (m, Ph), 1.26 (s, 18H, $C(CH_3)_3$) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 185.7 (C_{7a}), 155.2 (C_{7c}, C_{7j}), 132.5 (C_{7d}), 128.4 (C_{7e}, C_{7f}), 126.3 (C_{7g}, C_{7i}), 120.8 (C_{7h}), 108.9 (C_{7b}), 82.3 (C_{7k}), 29.6 (C_{7l}) ppm; MS (EI, 70 eV) *m/z* 781 (M^+); IR ν (KBr) = 3268, 2976, 2930, 1735, 1574, 1520, 1483, 1436, 1392, 1367, 1307, 1305, 1286, 1107, 1040, 1004, 937, 906, 840, 823, 783, 742, 720 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} 395 nm ($\varepsilon = 6.97\times10^4$ L mol^{-1} cm^{-1}); Mp. = 171-172 ºC; HRMS-ES (M^+) Calc'd. for $C_{42}H_{48}N_6O_9$ 781.3561, found 781.3541.

References

[1] Seto, C. T.; Mathias, J. P.; Whitesides, G. M. *J. Am. Chem. Soc*. **1993**, *115*, 1321.

[2] We have been unable to obtain satisfactory C analyses of these compounds or many related compounds we have prepared. In every case, even though ^{1}H NMR, ^{13}C NMR, and HR-MS of the compounds confirm purity, the C analysis is 1-2% low while the H and N analyses are very close. We are working on this problem, but are confident that it is an issue related to the combustion of these compounds. See Dai, Y.; Katz, T.J. *J. Org. Chem.* **1997**, *62*, 1274 (and references therein) for similar cases with conjugated oligomers and polymers, some containing salen-type ligands.