Tetraazacyclophanes by Palladium-Catalyzed Aromatic Amination. Stable, Geometrically Defined, High Spin Diradicals

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Supplementary Material

Experimental Procedures

General. All palladium-catalyzed reactions were assembled in the drybox in sealed reaction vessels and were heated in an oil bath at 100-110 °C. ^{1}H NMR spectra were acquired at 500 MHz using a Bruker AM-series spectrometer. Proton-decoupled ^{13}C spectra were similarly obtained at 125 MHz. Mass spectrometry analyses were performed by the Mass Spectrometry Facility at the University of Illinois at Urbana-Champaign. Analytical data were obtained from either Robertson Microlit Laboratories, Inc. or Atlantic Microlab Inc. Cyclic voltammetry utilized a Princeton Applied Research (PAR) VeraStat interfaced with a computer. A Ag/$AgNO_3$ reference electrode was used in conjunction with a carbon working electrode and a platinum counter electrode. The measurements were made on 2.0 mM solutions of macrocycle in 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane with and without 1% (by volume) added TFA, at a scan rate of 100 mV/sec. EPR measurements were performed on a Varian E-9 spectrometer, operating at 9.28 GHz, equipped with a TE_{102} cavity and an Oxford Instruments helium-flow cryostat, using 0.2 mM solutions of cyclophane in anhydrous dichloromethane with and without 1% (by volume) added TFA. The UV-vis oxidations utilized a Perkin Elmer Lambda 6 spectrophotometer. Toluene solvent was distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Palladium bis(dibenzylideneacetone) was prepared according to literature procedures. [1] *N,N'*-di(4-methoxyphenyl)-1,3-benzenediamine, **9**, was prepared from 4-methoxyaniline and 1,3-dibromobenzene in 64% yield as previously described. [2] Other chemicals were used as received from commercial suppliers.

General procedure for preparation of benzenediamines. In a dry box, 1,3-dibromobenzene or 1,4-dibromobenzene, the aryl amine (3.00 equiv), $Pd(OAc)_2$ (0.05 equiv.), bis(diphenylphosphinyl)ferrocene, (DPPF), (0.10 equiv) and sodium *tert*-butoxide (3.00 equiv) were combined in a large screw cap tube. A stir bar was added followed by toluene. The resulting mixture was removed from the dry box and stirred at 100-110 °C in an oil bath. The reaction was monitored by thin layer chromatography. After complete consumption of starting material, the reaction mixture was subjected to an aqueous work up, dried over magnesium sulfate ($MgSO_4$), and the solvent was evaporated under vacuum. The crude product was then purified by flash chromatography or recrystallization.

***N*,*N'*-di(4-Methylphenyl)-1,4-benzenediamine, 1**. The above general procedure was followed using 4-methylaniline (643 mg, 6.00 mmol) and 1,4-dibromobenzene (472 mg, 2.00 mmol) in 4 mL of toluene. After 10.5 h, the crude reaction mixture was treated with a saturated ammonium chloride solution and extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by flash chromatography using 75% toluene/hexanes to give 425 mg (74%) of **1** as a tan solid. ^1H NMR (500 MHz, C_6D_6) δ 2.15 (s, 6H), 4.86 (s, 2H), 6.81 (d, J = 8.2 Hz, 4H), 6.84 (s, 4H), 6.96 (d, J = 8.2 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 117.1, 120.3, 129.6, 129.8, 137.6, 142.0. Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.02; H, 7.08; N, 9.61.

***N*,*N'*-di(3-Methoxyphenyl)-1,4-benzenediamine, 2**. The above general procedure was followed using 3-methoxyaniline (369 mg, 3.00 mmol) and 1,4-dibromobenzene (236 mg, 1.00 mmol) in 2 mL of toluene. After 5 h, the crude reaction mixture was treated with a saturated ammonium chloride solution and extracted with toluene. The organic phase was washed with brine, dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by flash chromatography using 5% ethyl acetate/ toluene to give 208 mg (65%) of **2** as an off-white solid. ^1H NMR (500 MHz, C_6D_6) δ 3.33 (s, 6H), 4.92 (s, 2H), 6.43 (dd, J = 8.1 Hz, 2.0 Hz, 2H), 6.51 (dd, J = 8.0 Hz, 1.7 Hz, 2H), 6.54 (t, J = 2.2 Hz, 2H), 6.84 (s, 4H), 7.06 (t, J = 8.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.2, 102.1, 105.2, 109.0, 121.3, 130.1, 137.1, 145.9, 160.8. Anal Calcd for $C_{20}H_{20}N_2O_2$: C, 74.96; H, 6.29; N, 8.74. Found: C, 74.82; H, 6.30; N, 8.49.

***N*,*N'*-di(4-Methoxyphenyl)-1,4-benzenediamine, 3**. The above general procedure was followed using 4-methoxyaniline (369 mg, 3.00 mmol) and 1,4-dibromobenzene

(236 mg, 1.00 mmol) in 2 mL of toluene. After 5 h, the crude reaction mixture was treated with a saturated ammonium chloride solution and extracted with toluene. The organic phase was washed with brine, dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by flash chromatography using toluene then 5% ethyl acetate/toluene to give 144 mg (44%) of **3** as a tan solid. Alternatively, $Pd(dba)_2$ (23.0 mg, 0.04 mmol, 0.04 equiv) and P(*t*-Bu)$_3$ (6.5 mg, 0.03 mmol, 0.03 equiv) was used as catalyst and the reaction was stirred at room temperature. After 3 h, the crude reaction mixture was adsorbed directly onto silica gel and purified by flash chromatography using 3 % ethyl acetate/toluene to give 264 mg (83%) of **3** as a tan solid. ^{1}H NMR (500 MHz, C_6D_6) δ 3.35 (s, 6H), 4.73 (br s, 2H), 6.77 (d, *J* = 8.7 Hz, 4H), 6.80 (s, 4H), 6.83 (d, *J* = 8.7 Hz, 4H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 55.2, 114.5, 117.8, 118.2, 137.2, 138.2, 152.6. Anal Calcd for $C_{20}H_{20}N_2O_2$: C, 74.96; H, 6.29; N, 8.74. Found: C, 74.73; H, 6.28; N, 8.47.

***N,N'*-di(4-Methylphenyl)-1,3-benzenediamine, 7**. The above general procedure was followed using 4-methylaniline (1.61 g, 15.00 mmol) and 1,3-dibromobenzene (1.18 g, 5.00 mmol) in 10 mL of toluene. After 12 h, the crude reaction mixture was treated with 2% HCl and extracted with toluene. The organic phase was washed with brine, dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by flash chromatography using 20% ethyl acetate/hexanes to give 1.34 g (93%) of **7** as an off-white solid. Recrystallization from ethyl acetate/hexanes gave 1.05 g (74%) of product as white needles. ^{1}H NMR (500 MHz, C_6D_6) δ 2.12 (s, 6H), 4.95 (s, 2H), 6.48 (dd, *J* = 8.2 Hz, 2.0 Hz, 2H), 6.57 (t, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 4H), 6.94 (d, *J* = 8.0 Hz, 4H), 7.04 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6) δ 20.7, 105.4, 109.4, 119.6, 130.0, 130.3, 130.7, 140.9, 145.6. Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.37; H, 6.97; N, 9.78.

***N,N'*-di(3-Methoxyphenyl)-1,3-benzenediamine, 8**. The above general procedure was followed using 3-methoxyaniline (1.85 g, 15.00 mmol) and 1,3-dibromobenzene (1.20 g, 5.09 mmol) in 10 mL of toluene. After 12 h, the crude reaction mixture was treated with 2% HCl and extracted with toluene. The organic phase was washed with brine, dried over

$MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by flash chromatography using 20% ethyl acetate/hexanes to give 1.65 g (100%) of **8** as an orange oil. ^1H NMR (500 MHz, C_6D_6) δ 3.32 (s, 6H), 5.04 (s, 2H), 6.45 (dd *J* = 8.2 Hz, 2.3 Hz, 2H), 6.54 (dd, *J* = 8.0 Hz, 2.1 Hz, 2H), 6.58 (dd, *J* = 7.8 Hz, 2.0 Hz, 2H), 6.61 (t, *J* = 2.2 Hz, 2H), 6.67 (t, *J* = 2.0 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, C_6D_6) δ 54.7, 104.5, 106.8, 107.7, 111.0, 111.1, 130.2, 130.3, 144.6, 144.8, 161.3. HRMS (EI) Calcd for $C_{20}H_{20}N_2O_2$: 320.1525. Found: 320.1528.

***tert*-Butyl 4-{3-[4-(*tert*-butoxycarbonyl)anilino]anilino}benzoate, 10**. In a dry box, 1,3-phenylenediamine (110 mg, 1.00 mmol, 1.00 equiv) was combined with $Pd(dba)_2$ (11.5 mg, 0.02 mmol, 0.02 equiv), tri-*t*-butylphosphine (3.2 mg, 0.16 mmol, 0.16 equiv) and sodium *tert*-butoxide (144 mg, 1.50 mmol, 1.50 equiv). A solution of *tert*-butyl 4-bromobenzoate (515 mg, 2.00 mmol, 2.00 equiv) in toluene (1.5 mL), followed by an additional 1.5 mL of toluene, was added to give a brown mixture. A stir bar was added and the sealed vial was stirred at room temperature. After 24 h, the crude reaction mixture (a green slurry) was poured into a saturated ammonium chloride solution and extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was chromatographed with 15% ethyl acetate/hexanes to give 299 mg (65%) of **10** as an off-white solid. ^1H NMR (500 MHz, CD_2Cl_2) δ 1.56 (s, 18H), 6.14 (s, 2H), 6.83 (dd, *J* = 8.0 Hz, 2.1 Hz, 2H), 6.96 (t, *J* = 2.0 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 4H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.3, 80.3, 110.3, 113.7, 115.2, 123.6, 130.4, 131.2, 142.5, 147.0, 165.7. HRMS Calcd for $C_{28}H_{32}N_2O_4$: 460.2362. Found: 460.2354.

General procedure for reaction of benzenediamines 7-10 with 1,4-dibromobenzene. In a dry box, the benzenediamine , 1,4-dibromobenzene (10.0 equiv), $Pd(OAc)_2$ (0.040 equiv), DPPF (0.080 equiv) and sodium *tert*-butoxide (3.00 equiv) were combined in a large screw cap tube or a Schlenk flask. A stir bar was added followed by toluene. The resulting mixture was stirred at 100-110 °C in an oil bath. After consumption of starting materials, the reaction mixture was subjected to aqueous workup, dried over $MgSO_4$, and the solvent was evaporated under vacuum. The excess 1,4-dibromobenzene was removed by Kugelrohr distillation, and the residue was purified by recrystallization or flash chromatography.

***N1,N3*-di-(4-Bromophenyl)-*N1,N3*-di(4-methylphenyl)-1,3-benzenediamine, 11**. The above general procedure was followed using 1.00 g (3.47 mmol, 1.00 equiv) of *N,N'*-di(4-methylphenyl)-1,3-benzenediamine and 1,4-dibromobenzene (8.20 g, 34.70 mmol, 10.00 equiv) in 35 mL of toluene. After 24 h, the crude product was treated with a saturated ammonium chloride solution and extracted with chloroform. The combined organic phase was washed with brine and dried over $MgSO_4$. The excess 1,4-dibromobenzene was removed by Kugelrohr distillation, and the residue was purified by recrystallization from ethyl acetate/dichloromethane to give 1.53 g (73%) of **11** as a white solid. ^1H NMR (500 MHz, C_6D_6) δ 2.05 (s, 6H), 6.65 (dd, *J* = 8.1 Hz, 2.0 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 4H), 6.81 (d, *J* = 8.2 Hz, 4H), 6.87-6.91 (m, 6H), 7.08 (d, *J* = 8.7 Hz, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 20.7, 115.0, 117.9, 119.2, 125.1, 125.4, 130.3, 130.4, 132.4, 133.5, 144.8, 147.1, 149.0. Anal. Calcd for $C_{32}H_{26}N_2Br_2$: C, 64.23; H, 4.38; N, 4.68. Found: C, 64.23; H, 4.50; N, 4.62.

***N1,N3*-di-(4-Bromophenyl)-*N1,N3*-di-(3-methoxphenyl)-1,3-benzenediamine, 12**. The above general procedure was followed using 1.23 g (3.83 mmol, 1.00 equiv) of *N,N'*-di(3-methoxyphenyl)-1,3-benzenediamine and 1,4-dibromobenzene (9.03 g, 38.29 mmol, 10.00 equiv) in 38 mL of toluene. After 24 h, the crude product was treated with a saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic phase was washed with brine and dried over $MgSO_4$. The excess 1,4-dibromobenzene was removed by Kugelrohr distillation, and the residue was purified by flash chromatography using 25% toluene/hexanes to give 1.80 g (75%) of **12** as an off-white solid. Recrystallization from ethyl acetate/dichloromethane gave 1.56 g (65%) of **12** as a white solid. ^1H NMR (500 MHz, C_6D_6) δ 3.19 (s, 6H), 6.44 (dd, *J* = 8.2 Hz, 2.4 Hz, 2H), 6.60 (dd, *J* = 8.0 Hz, 1.9 Hz, 2H), 6.65 (dd, *J* = 7.4 Hz, 1.9 Hz, 2H), 6.72-6.74 (m, 6H), 6.87 (t, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 8.1 Hz, 2H), 6.97 (br s, 1H), 7.08 (d, *J* = 8.6 Hz, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 54.7, 109.2, 110.8, 115.7, 117,1, 118.8, 120.1, 125.9, 130.3, 130.4, 132.5, 146.8, 148.6, 148.7, 161.2. Anal. Calcd for $C_{32}H_{26}N_2O_2Br_2$: C, 60.97; H, 4.16; N, 4.44. Found: C, 60.91; H, 4.20; N, 4.42.

***N1,N3*-di-(4-Bromophenyl)-*N1,N3*-di-(4-methoxyphenyl)-1,3-benzenediamine, 13**. The above general procedure was followed using 1.20 g (3.74 mmol, 1.00 equiv) of *N,N'*-di(4-methoxyphenyl)-1,3-benzenediamine and 1,4-dibromobenzene (8.84 g, 37.45 mmol, 10.00 equiv) in 37 mL of toluene. After 24 h, the crude product was treated with a saturated ammonium chloride solution and extracted with toluene. The combined organic phase was washed with brine and dried over $MgSO_4$. The excess 1,4-dibromobenzene was removed by Kugelrohr distillation, and the residue was purified by flash chromatography using 5% ethyl acetate/hexanes to 50% ethyl acetate/hexanes. Recrystallization from ethyl acetate gave 1.88 g (79%) of **13** as an off-white solid. ^1H NMR (500 MHz, C_6D_6) δ 3.26 (s, 6H), 6.61-6.66 (m, 6H), 6.75 (d, J = 8.7 Hz, 4H), 6.89-6.93 (m, 6H), 7.11 (d, J = 8.7 Hz, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 55.0, 114.5, 115.2, 117.0, 118.0, 124.4, 127.6, 130.2, 132.32, 140.2, 147.3, 149.1, 157.1. Anal. Calcd for $C_{32}H_{26}N_2O_2Br_2$: C, 60.97; H, 4.16; N, 4.44. Found: C, 60.69; H, 4.19; N ,4.32.

***tert*-Butyl 4-[3-{4-bromo[4-(*tert*-butoxycarbonyl)phenyl]anilino}(4-bromophenyl)anilino]benzoate, 14**. The above general procedure was followed using 922 mg (2.00 mmol, 1.00 equiv) of *tert*-butyl 4-{3-[4-(*tert*-butoxycarbonyl)anilino]anilino}benzoate and 1,4-dibromobenzene (4.72 g, 20.02 mmol, 10.00 equiv) in 20 mL of toluene. After 85 h, the crude product was treated with a saturated ammonium chloride solution and extracted with toluene. The combined organic phase was washed with brine and dried over $MgSO_4$. The excess 1,4-dibromobenzene was removed by Kugelrohr distillation, and the residue was purified by flash chromatography using 5% ethyl acetate/hexanes to give 1.16 g (75%) of **14** as a white foam solid. A portion was recrystallized from ethyl acetate/hexanes for elemental analysis. ^1H NMR (500 MHz, C_6D_6) δ 1.50 (s, 18 H), 6.58-6.62 (m, 6 H), 6.81-6.87 (m, 6H), 7.08 (d, J = 8.6 Hz, 4H), 8.00 (d, J = 8.6 Hz, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 28.2, 80.2, 117.2, 120.3, 121.6, 121.7, 126.5, 126.9, 130.7, 131.3, 132.8, 145.9, 148.1, 150.7, 165.1. Anal. Calcd for $C_{40}H_{38}N_2O_4Br_2$: C, 62.35; H, 4.97; N, 3.64. Found: C, 62.41; H, 4.95; N, 3.75.

General procedure for preparation of compounds 15-17. In a drybox, the dibromide, the aryl amine (3.00 equiv), $Pd(OAc)_2$ (0.04 equiv), DPPF (0.08 equiv) and sodium *tert*-butoxide (3.00 equiv) were combined in a large screw cap tube. A stir bar was added followed by toluene. The resulting mixture was removed from the dry box and stirred at 100-110 °C in an oil bath. After consumption of starting materials, the reaction mixture was treated with a saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic phase was sequentially washed with a 2% HCl solution, a saturated $NaHCO_3$ solution, and finally with brine. The organic phase was dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by flash chromatography.

***N1,N3*-di{4-(4-Methylanilino)phenyl}-*N1,N3*-di(4-methylphenyl)-1,3-benzenediamine, 15**. The above general procedure was followed using **11** (598 mg, 1.00 mmol, 1.00 equiv), 4-methylaniline (321 mg, 3.00 mmol, 3.00 equiv) in 10 mL of toluene. After 3 h, the reaction mixture was subjected to the aqueous workup. The crude product was purified by flash chromatography using 10% ethyl acetate/hexanes to give 616 mg (95%) of **15** as a tan foam solid. ^1H NMR (500 MHz, C_6D_6) δ 2.06 (s, 6H), 2.14 (s, 6H), 4.86 (s, 2H), 6.71 (d, J = 8.6 Hz, 4H), 6.78-6.82 (m, 6H), 6.88 (d, J = 8.2 Hz, 4H), 6.93 (d, J = 8.2 Hz, 4H), 7.00 (t, J = 8.0 Hz, 1H), 7.06 (d, J = 8.8 Hz, 4H), 7.14-7.20 (m overlapping solvent, 5H). ^{13}C NMR (125 MHz, C_6D_6) δ 20.69, 20.74, 116.0, 117.0, 118.3, 118.9, 124.4, 126.8, 130.0, 130.1, 131.8, 139.8, 141.3, 141.4, 146.0, 150.0, 2 carbons not observed. HRMS Calcd for $C_{46}H_{42}N_4$: 650.3410. Found: 650.3411.

***N1,N3*-di{4-(3-Methoxyanilino)phenyl}-*N1,N3*-di(3-methoxyphenyl)-1,3-benzenediamine, 16**. The above general procedure was followed using **12** (630 mg, 1.00 mmol, 1.00 equiv), 3-methoxyaniline (369 mg, 3.00 mmol, 3,00 equiv) in 10 mL of toluene. After 9 h, the reaction mixture was subjected to the aqueous workup. The crude product was purified by flash chromatography using 20% ethyl acetate/hexanes to give 690 mg (97%) of **16** as an off-white foam solid. ^{1}H NMR (500 MHz, C_6D_6) δ 3.22 (s, 6H), 3.33 (s, 6H), 5.01 (s, 2H), 6.41-6.43 (m, 2H), 6.46-6.49 (m, 4H), 6.53 (t, *J* = 2.2 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 4H), 6.82-6.84 (m, 4H), 6.90 (t, *J* = 2.2 Hz, 2H), 6.96-7.05 (m, 9H), 7.20 (t, *J* = 2.1 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6) δ 54.7, 54.8, 103.5, 106.1, 108.3, 109.6, 110.1, 116.3, 117.4, 118.7, 120.0, 127.0, 130.1, 130.3, 139.1, 141.5, 145.4, 149.3, 149.6, 161.1, 161.3, one carbon not observed. HRMS Calcd for $C_{46}H_{42}N_4O_4$: 714.3206. Found: 714.3207.

***N1,N3*-di{4-(4-Methoxyanilino)phenyl}-*N1,N3*-di(4-methoxyphenyl)-1,3-benzenediamine, 17**. The above general procedure was followed using **13** (630 mg, 1.00 mmol, 1.00 equiv), 4-methoxyaniline (369 mg, 3.00 mmol, 3.00 equiv) in 10 mL of toluene. After 5.5 h, the reaction mixture was subjected to the aqueous workup. The crude product was purified by flash chromatography using 30% ethyl acetate/hexanes to give 613 mg (86%) of **17** as an off-white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 3.27 (s, 6H), 3.35 (s, 6H), 4.73 (s, 2H), 6.66-6.68 (m, 8H), 6.74-6.78 (m, 6H), 6.80-6.84 (m, 4H), 7.03 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 4H), 7.13-7.15 (m, overlapping with solvent, 5H). ^{13}C NMR (125 MHz, C_6D_6) δ 55.0, 55.1, 114.3, 114.9, 114.98, 115.0, 117.7, 121.3, 126.5, 126.7, 129.9, 136.9, 140.9, 141.0, 141.6, 150.1, 155.4, 156.2. HRMS Calcd for $C_{46}H_{42}N_4O_4$: 714.3206. Found: 714.3207.

***tert*-Butyl4-{3-{4-(*tert*-butoxycarbonyl)[4-(4-methoxyanilino)phenyl]anilino}[4-(4-methoxyanilino)phenyl]anilino} benzoate, 18**. In a dry box, **14** (100 mg, 0.13 mmol, 1.00 equiv) was combined with 4-methoxyaniline (48 mg, 0.39 mmol, 3.00 equiv), Pd(dba)$_2$ (3.0 mg, 5.2 μmol, 0.04 equiv), tri-*t*-butylphosphine (0.84 mg, 4.2 μmol, 0.032 equiv) and sodium *tert*-butoxide (37 mg, 0.39 mmol, 3.00 equiv) in a vial. A stir bar was added followed by 1 mL of toluene to give a purple mixture that quickly became brown. The reaction mixture was removed from the box and stirred at room temperature. After 24 h, the reaction mixture was adsorbed onto silica gel and purified by flash chromatography using 30% ethyl acetate/hexanes to give 102 mg (91%) of **14** as a yellow oil. ^{1}H NMR (500 MHz, C_6D_6) δ 1.48 (s, 18H), 3.35 (s, 6H), 4.89 (s, 2H), 6.61 (d, *J* = 8.8 Hz, 4H), 6.78 (d, *J* =

8.8 Hz, 4H), 6.81 (dd, *J* = 8.0 Hz, 2.1 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 4H), 6.96 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 4H), 7.14 (t, *J* = 2.0 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 28.1, 54.9, 79.6, 114.9, 116.6, 119.2, 119.6, 120.5, 122.5, 124.3, 127.6, 130.2, 131.0, 135.7, 138.2, 143.1, 148.3, 151.7, 155.8, 165.4. HRMS Calcd for $C_{54}H_{54}N_4O_6$: 854.4043. Found: 854.4042.

***tert*-Butyl-4-(benzylamino) benzoate, 19**. In a dry box, *tert*-butyl 4-bromobenzoate (2.00 g, 7.78 mmol, 1.00 equiv) was combined with benzylamine (1.70 g, 15.6 mmol, 2.00 equiv), $Pd(OAc)_2$ (35 mg, 0.15 mmol, 0.020 equiv), DPPF (172 mg, 0.31 mmol, 0.040 equiv) and sodium *tert*-butoxide (1.10 g, 11.67 mmol, 1.50 equiv)in a large tube. A stir bar was added followed by 25 mL of toluene. The resulting mixture was removed from the box and stirred at 100-110 °C. After 18 h, the reaction mixture was treated with a saturated ammonium chloride solution and extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by flash chromatography using 10% ethyl acetate/hexanes to give 1.46 g (66%) of **19** as an off-white solid that became light orange on standing. ^{1}H NMR (500 MHz, C_6D_6) δ 1.48 (s, 9H), 3.84 (d, *J* = 5.5 Hz, 2H), 3.93 (br s, 1H), 6.29 (d, *J* = 8.1 Hz, 2H), 7.02-7.13 (m, 5H), 8.09 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, C_6D_6) δ 28.3, 47.4, 79.3, 111.9, 121.1, 127.4, 127.5, 128.8, 131.7, 139.0, 151.7, 166.1. Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.28; H, 7.44; N, 4.94.

***tert*-Butyl4-(3-{4-[benzyl-4-(*tert*-butoxycarbonyl)anilino][4-*tert*-butoxycarbonyl)phenyl]anilino}{4-[benzyl-4-(*tert*-butoxycarbonyl)anilino]phenyl}anilino)benzoate, 20**. In a dry box, **14** (1.00 g, 1.30 mmol, 1.10 equiv) was combined with *tert*-butyl-4-(benzylamino)benzoate (0.67 g, 2.36 mmol, 2.00 equiv), $Pd(dba)_2$ (27.0 mg, 0.047 mmol, 0.04 equiv), tri-*t*-butylphosphine (7.6 mg, 0.038 mmol, 0.032 equiv) and sodium *tert*-butoxide (0.34 g, 3.54 mmol, 3.00 equiv) in a vial. A stir bar was added followed by 13 mL of toluene. The reaction mixture was removed from the box and stirred at room temperature. After 24 h, the reaction mixture was treated with a saturated ammonium chloride solution and extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by flash chromatography using 5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes to give 1.20 g (86%) of **20** as a yellow solid. ^1H NMR (500 MHz, C_6D_6) δ 1.47 (s, 18H), 1.49 (s, 18H), 4.60 (s, 4H), 6.75 (dd, *J* = 8.0 Hz, 2.1 Hz, 2H), 6.78 (d, *J* =1.8 Hz, 4H), 6.88-6.93 (m, 9H), 6.98 (d, *J* = 8.8 Hz, 4H), 7.02-7.05 (m, 3H), 7.12-7.13 (m, 8H), 8.04 (d, *J* = 8.8 Hz, 4H), 8.10 (d, *J* = 8.9 Hz, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 28.2, 28.3, 56.2, 79.6, 80.1, 115.6, 120.2, 121.3, 121.6, 123.1, 125.9, 126.3, 126.8, 126.9, 127.3, 128.9, 130.7, 131.3, 131.5, 138.5, 143.2, 143.6, 148.4, 151.2, 151.4, 165.2, 165.5. HRMS Calcd for $C_{76}H_{78}N_4O_8$: 1174.5820. Found: 1174.5814. Anal Calcd for $C_{76}H_{78}N_4O_8$: C, 77.66; H, 6.69; N, 4.77. Found: C, 77.63; H, 6.77; N, 4.56.

***tert*-Butyl4-(3-{4-[4-(*tert*-butoxycarbonyl)anilino][4-(*tert*-butoxycarbonyl)phenyl]anilino}{4-[4-(*tert*-butoxycarbonyl)anilino]phenyl} anilino)benzoate), 21**. A solution of **20** (1.10 g, 0.94 mmol) in 100 mL of tetrahydofuran: ethanol (1:1), was added to a flask containing 10% palladium on carbon (110 mg, 10% by weight). The mixture was stirred under a balloon filled with hydrogen. After 3 days, an additional 110 mg of 10% palladium on carbon was added. After a total of 7 days, the black suspension was filtered through celite, and the solvent was removed under vacuum to give **22** as a yellow foam solid. The crude product was recrystallized from ethyl acetate/hexanes to give 768 mg (83%) of **21** as a white solid. Reaction on a 0.11 mmol scale required only 10% by weight of palladium on carbon, and the reaction time was ca. 36 h. ^1H NMR (500 MHz, C_6D_6) δ 1.47 (s, 18H), 1.50 (s, 18H), 5.62 (s, 2H), 6.76 (d, *J* = 8.4 Hz, 8H), 6.80 (dd, *J* = 8.1 Hz, 2.1 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 4H), 6.97-7.04 (m, 5H), 7.07 (t, *J* = 2.0 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 4H), 8.14 (d, *J* = 8.7 Hz, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 28.2, 28.3, 79.8, 80.1, 115.2, 119.7, 120.7, 121.0, 121.3, 124.1, 125.5, 127.5, 130.6, 131.3, 131.7, 138.5, 141.3, 147.6, 148.5, 151.5. Anal. Calcd for $C_{62}H_{66}N_4O_8$: C, 74.82; H, 6.69; N, 5.63. Found: C, 74.74; H, 6.73; N, 5.37.

General procedure for preparation of tetraazacyclophanes using stepwise synthesis. In a dry box, 1,3-dibromobenzene was combined with the tetraamine (1.00 equiv), Pd(dba)$_2$ (0.040 equiv), tri-*t*-butylphosphine (0.032 equiv) and sodium *tert*-butoxide (3.00 equiv) in a vial. A stir bar was added followed by toluene. The reaction mixture was removed from the box and stirred at room temperature, typically for 24 h. The crude product was adsorbed onto silica gel and purified by flash chromatography.

4-Tolyl-tetraazacyclophane, 4. The above general procedure was followed using **15** (130 mg, 0.200 mmol) in 20 mL of toluene. After 24 h, the mixture was adsorbed onto silica gel and purified by flash chromatography using 50% hexanes/toluene to give 104 mg (72%) of **4** as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 2.08 (s, 12H), 6.66 (t, *J* = 2.0 Hz, 2H), 6.76 (dd, *J* = 8.0 Hz, 2.1 Hz, 4H), 6.85 (s, 8H), 6.88 (d, *J* = 8.2 Hz, 4H), 6.93 (t, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 20.7, 115.0, 116.0, 125.6, 126.2, 129.8, 130.2, 132.7, 143.4, 145.2, 149.8. MALDI-TOF m/z 724.5. Anal Calcd for $C_{52}H_{44}N_4$: C, 86.15; H, 6.12; N, 7.73. Found: C, 85.89; H, 6.28; N, 7.46.

3-Anisyl-tetraazacyclophane, 5. The above general procedure was followed using **16** (143 mg, 0.200 mmol) in 20 mL of toluene. After 24 h, the mixture was adsorbed onto silica gel and purified by flash chromatography using neat toluene to give 95 mg (60%) of **5** as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 3.20 (s, 12H), 6.52 (dd, *J* = 8.0 Hz, 2.3 Hz, 4H), 6.58 (t, *J* = 2.2 Hz, 2H), 6.82-6.83 (m, 12H), 6.87-6.92 (m, 6H), 6.97-7.00 (m, 8H). ^{13}C NMR (125 MHz, C_6D_6) δ 54.7, 109.2, 110.8, 116.0, 117.2, 117.6, 126.4, 129.8, 130.2, 143.3, 148.8, 149.5, 161.2. MALDI-TOF m/z 788.6. Anal Calcd for $C_{52}H_{44}N_4O_4$: C, 79.16; H, 5.62; N, 7.10. Found: C, 78.99; H, 5.66; N, 6.95.

4-Anisyl-tetraazacyclophane, 6. The above general procedure was followed using **17** (143 mg, 0.200 mmol) in 20 mL of toluene. After 48 h, the mixture was adsorbed onto silica gel and purified by flash chromatography using 2% ethyl acetate/toluene to give 83 mg (53%) of **6** as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 3.26 (s, 12H), 6.68-6.70 (m, 12H), 6.77 (t, *J* = 2.2 Hz, 2H), 6.89 (s, 8H), 6.97 (t, *J* = 8.0 Hz, 2H), 7.2 (d, *J* = 8.9 Hz, 8H). ^{13}C NMR (125

MHz, C_6D_6) δ 55.0, 113.8, 114.0, 115.1, 125.9, 127.7, 130.0, 140.6, 143.3, 150.1, 156.7. MALDI-TOF m/z 788.7. Anal Calcd for $C_{52}H_{44}N_4O_4$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.07; H, 5.76; N, 6.93.

Mixed tetraazacyclophane, 22. The above general procedure was followed using **18** (94.8 mg, 0.11 mmol) and 1,3-dibromobenzene (26.2 mg, 0.20 mmol, 1.00 equiv) in 11 mL of toluene. After 24 h, the mixture was adsorbed onto silica gel and purified by flash chromatography using toluene then 5% ethyl acetate/toluene to give 40 mg (39%) of **23** as faint yellow solid. When the reaction was repeated on a larger scale (0.29 mmol of **18**), the product was obtained in 67% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.56 (s, 18H), 3.79 (s, 6H), 6.25 (t, *J* = 2.0 Hz, 1H), 6.33 (t, *J* = 2.0 Hz, 1H), 6.42 (dd, *J* = 8.1 Hz, 2.2 Hz, 2H), 6.85-6.89 (m, 14 H), 6.96 (t, *J* = 8.1 Hz, 1H), 7.11-7.18 (m, 9H), 7.82 (d, *J* = 8.9 Hz, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 28.2, 55.0, 80.0, 114.1, 115.3, 117.9, 119.9, 122.4, 126.2, 126.4, 126.5, 127.6, 129.9, 130.1, 131.3, 140.5, 142.1, 144.5, 148.8, 150.0, 150.9, 157.0, 165.3, one carbon not observed. MALDI-TOF m/z 928.7. Anal Calcd for $C_{60}H_{56}N_4O_6$: C, 77.56; H, 6.07; N, 6.03. Found: C, 77.28; H, 6.10; N, 5.93.

4-*tert*-Butoxycarbonyl-tetraazacyclophane, 23 The above general procedure was followed using **22** (338 mg, 0.339 mmol) and 1,3-dibromobenzene (80 mg, 0.339 mmol, 1.00 equiv) in 39.0 mL of toluene. After 24 h, the mixture was adsorbed onto silica gel and purified by flash chromatography using 2% ethyl acetate/toluene give 275 mg (76%) of **23** as a faint yellow solid. ^{1}H NMR (500 MHz, C_6D_6) δ 1.44 (s, 36H), 6.32 (br s, 2H), 6.70 (s, 8H), 6.82-6.88 (m, 6H), 7.20 (d, *J* = 8.6 Hz, 8H), 8.14 (d, *J* = 8.6 Hz, 8H). ^{13}C NMR (125 MHz, C_6D_6) δ 28.2, 80.1, 118.1, 120.1, 122.2, 126.4, 126.8, 130.0, 131.4, 143.2, 148.6, 150.7, 165.2. MALDI-TOF m/z 1068.4. Anal Calcd for $C_{68}H_{68}N_4O_8$: C, 76.40; H, 6.41; N, 5.24. Found: C, 76.16; H, 6.51; N, 5.16.

General procedure for preparation of tetraazacyclophane 4-6 using one-step synthesis. In a dry box, 1,3-dibromobenzene was combined with the benzenediamine (1.00 equiv), $Pd(OAc)_2$ (0.05 equiv), tri-*t*-butylphosphine (0.04 equiv) and sodium *tert*-butoxide (3.00

equiv) in a 500 mL Schlenk flask. A stir bar was added followed by 250 mL of toluene. The sealed flask was removed from the box and stirred room temperature for typically 2-5 days. The crude product was poured into water and the organic phase was dried over $MgSO_4$. The solvent was removed under vacuum and the crude product was purified by preparative thin layer chromatography (PTLC) or by flash chromatography.

4-Tolyl-tetraazacyclophane, 4. The above general procedure was followed using **1** (72.0 mg, 0.25 mmol) with 1,3-dibromobenzene (59.0 mg, 0.25 mmol, 1.00 equiv) in 250 mL of toluene. After 5 days, the reaction solution was subjected to the aqueous workup. The crude product was purified by flash chromatography using 30% toluene/hexanes to give 51 mg (56%) of **4** as a white solid identical to the material prepared by the stepwise synthesis.

3-Anisyl-tetraazacyclophane, 5. The above general procedure was followed using **2** (80.0 mg, 0.25 mmol) with 1,3-dibromobenzene (59.0 mg, 0.250 mmol, 1.00 equiv) in 250 mL of toluene. After 5 days, the reaction solution was subjected to the aqueous workup. The crude product was purified by PTLC using toluene to give 46 mg (47%) of **5** as a white solid identical to the material prepared by the stepwise synthesis.

4-Anisyl-tetraazacyclophane, 6. The above general procedure was followed using **3** (80.0 mg, 0.25 mmol) with 1,3-dibromobenzene (59.0 mg, 0.25 mmol, 1.00 equiv) in 250 mL of toluene. After 5 days, the reaction solution was subjected to the aqueous workup. The crude product was purified by flash chromatography using 2% ethyl acetate/toluene to give 31 mg (31%) of **6** as a white solid identical to the material prepared by the stepwise synthesis.

Oxidation of Tetraazacyclophanes with Bis(trifluroacetoxy)iodobenzene, General Procedure. In a dry box, 5.0 µmol of tetraazacyclophane was weighed into a 10.0 mL volumetric flask. The flask was filled with dichloromethane to give a 0.50 mM solution. This solution was diluted 1:10 and 2 mL of this solution was placed into a Uv-vis cuvette. Increments of between 2.0 to 5.0 µL (0.02-0.05 µmol, 0.20-0.50 equiv) of a 0.010 M solution of bis(trifluroacetoxy)iodobenzene in dichloromethane were added to the tetraazacyclophane solution in the drybox. The cuvette was removed from the drybox after each addition and the oxidation was monitored by Uv-vis spectroscopy.

Magnetic Susceptibility Measurements, General Procedure. In a dry box, 10.0 mg of cyclophane was weighed into a 1.0 mL volumetric flask, and the flask was filled with dichloromethane. To 0.50 mL of this solution was added two or four equivalents of PIFA (as a 0.20 or a 0.40 M solution in dichloromethane), and 50.0 μL of TFA. The resulting dark green solution was syringed into a screw capped NMR tube. A coaxial tube (I.D. 2 mm) containing dichloromethane with added 10 % TFA was placed inside the NMR tube. The sealed tube was removed from the drybox, and the difference in ^{1}H NMR chemical shift of the dichloromethane / TFA solvent resonamces was measured at 500 MHz after one pulse. The identical procedure was followed without added TFA.

1) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1982**, *28*, 110-113.

(2) Goodson, F. E.; Hartwig, J. F. *Macromolecules* **1998**, *31*, 1700-1703.

Crystal Data and Structure Refinement for 4

Data Collection

A colorless needle crystal of $C_{52}H_{44}N_4{}^{\bullet}(C_7H_8)_{0.80}$ having approximate dimensions of 0.08 x 0.10 x 0.25 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1^{o} in ω, 10s exposure, de-zingered) data frames, corresponded to a primitive orthorhombic cell with dimensions: a = 9.0095(2) Å, b = 18.2587(4) Å, c = 28.416(1) Å and V = 4674.4(2) Å3. For Z = 4 and F.W. = 798.66, the calculated density is 1.13 g/cm^3. Based on the systematic absences of: 0kl: k+l = 2n+1, hk0: h = 2n+1; packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: Pnma (#62). In this space group the molecule and the solvent in the lattice are located on a crystallographic mirror plane.

The data were collected at a temperature of 23 $\pm$ 1^{o}C to a maximum 2θ value of 61.0^{o}. One phi scan consisting of 182 data frames was collected with a scan width of 1^{o} and a detector-to-crystal distance, Dx, of 35mm. Each frame was exposed twice (for the purpose of de-zingering) for 90s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, “Processing of X-Ray Diffraction Data Collected in Oscillation Mode,” Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

A total of 7824 reflections was collected. No decay correction was applied. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.7 cm^{-1} and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. In the case of the methyl group hydrogen atoms, one hydrogen was located in the difference map and included at an idealized distance to set the orientation of the other two hydrogen atoms. The occupancy of the toluene solvent was refined to be 80 per cent. The final cycle of full-matrix least-squares refinement[3] was based on 2883 observed reflections ($I > 5.00\sigma(I)$) and 295 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.056$$

$$Rw = [(\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo2)]^{1/2} = 0.063$$

The standard deviation of an observation of unit weight[4] was 3.72. The weighting scheme was based on counting statistics and included a factor ($p = 0.010$) to downweight the intense reflections. Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.37 and -0.24 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G.; *J. Appl. Cryst.,* 27, 435-436 (1994).

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

3) Least-Squares:

Function minimized Σ*w*(|Fo|-|Fc|)2

where w =1/_s2(Fo)

and _2(Fo) = [S2(C+R2B) + (pFo2)2]/Lp2

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarization factor

p = p-factor

4) Standard deviation of an observation of unit weight:

[_w(|Fo|-|Fc|)2/(No-Nv)]1/2

where N_O = number of observations and N_V = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

Experimental Details for 4

A. Crystal Data

Empirical Formula	$C_{57.60}H_{50.40}N_4$
	$C_{52}H_{44}N_4{}^{\bullet}(C_7H_8)_{0.80}$
Formula Weight	798.66
Crystal Color, Habit	colorless, needle
Crystal Dimensions	0.08 X 0.10 X 0.25 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 9.0095(2)Å
	b = 18.2587(4) Å
	c = 28.416(1) Å
	V = 4674.4(2) Å^3
Space Group	Pnma (#62)
Z value	4
Dcalc	1.135 g/cm^3
F000	1696.00
μ(MoKα)	0.66 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
Take-off Angle	2.8^{o}
Crystal to Detector Distance	35 mm
Temperature	23.0^{o}C
Scan Rate	90sec/frame
Scan Width	1^{o}/frame

2θmax	61.0°
No. of Reflections Measured	Total: 7824
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w (\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$1/\sigma^2(Fo)$
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>5.00\sigma(I)$)	2883
No. Variables	295
Reflection/Parameter Ratio	9.77
Residuals: R; Rw	0.056 ; 0.063
Goodness of Fit Indicator	3.72
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.37 e-/Å^3
Minimum peak in Final Diff. Map	-0.24 e-/Å^3

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
N(1)	0.3701(2)	0.1171(1)	0.13668(6)	4.05(5)
N(2)	0.2559(2)	0.1169(1)	-0.05877(6)	3.94(5)
C(1)	0.3444(3)	0.1133(1)	0.08724(8)	3.23(6)
C(2)	0.2252(3)	0.0749(1)	0.06895(8)	3.81(6)
C(3)	0.1974(3)	0.0747(1)	0.02077(8)	3.80(6)
C(4)	0.2891(3)	0.1125(1)	-0.01013(8)	3.28(6)
C(5)	0.4112(2)	0.1483(1)	0.00836(8)	3.40(6)
C(6)	0.4379(2)	0.1489(1)	0.05609(8)	3.50(6)
C(7)	0.3435(3)	0.0549(1)	0.16566(8)	3.51(6)
C(8)	0.2824(3)	0.0628(1)	0.21034(8)	4.11(6)
C(9)	0.2530(3)	0.0026(2)	0.23772(9)	4.61(7)
C(10)	0.2812(3)	-0.0675(2)	0.22214(9)	4.64(7)
C(11)	0.3425(3)	-0.0749(1)	0.17785(9)	4.60(7)
C(12)	0.3754(3)	-0.0150(1)	0.15006(9)	4.30(7)
C(13)	0.2449(4)	-0.1334(2)	0.2522(1)	7.7(1)
C(14)	0.2089(3)	0.0547(1)	-0.08468(8)	3.28(6)
C(15)	0.2667(3)	-0.0141(1)	-0.07608(9)	4.07(7)
C(16)	0.2206(3)	-0.0734(1)	-0.10256(10)	4.37(7)
C(17)	0.1189(3)	-0.0666(1)	-0.13845(8)	3.62(6)
C(18)	0.0621(3)	0.0021(1)	-0.14680(8)	3.85(6)
C(19)	0.1041(3)	0.0619(1)	-0.12022(8)	3.77(6)
C(20)	0.0685(3)	-0.1326(1)	-0.16676(10)	5.56(8)
C(21)	0.3665(4)	0.2500	0.1402(1)	3.60(8)
C(22)	0.4202(3)	0.1840(1)	0.15681(8)	3.62(6)
C(23)	0.5239(3)	0.1844(1)	0.19301(9)	4.52(7)
C(24)	0.5718(4)	0.2500	0.2110(1)	5.0(1)
C(25)	0.2509(3)	0.2500	-0.0613(1)	3.43(8)
C(26)	0.2846(3)	0.1839(1)	-0.08263(8)	3.21(6)
C(27)	0.3484(3)	0.1840(1)	-0.12713(8)	3.60(6)
C(28)	0.3777(4)	0.2500	-0.1489(1)	3.79(9)
C(29)	-0.2479(9)	0.2500	-0.0770(3)	10.3(3)
C(30)	-0.2138(6)	0.1840(4)	-0.0563(3)	10.4(2)
C(31)	-0.1469(6)	0.1836(3)	-0.0159(3)	9.2(2)
C(32)	-0.1126(7)	0.2500	0.0059(2)	8.7(3)
C(33)	-0.034(1)	0.2500	0.0463(4)	15.2(4)
H(1)	0.1616	0.0484	0.0895	4.5732
H(2)	0.1147	0.0483	0.0088	4.5576
H(3)	0.4779	0.1728	-0.0122	4.0740
H(4)	0.5222	0.1743	0.0679	4.1972
H(5)	0.2608	0.1104	0.2220	4.9325
H(6)	0.2121	0.0094	0.2682	5.5332
H(7)	0.3626	-0.1226	0.1662	5.5151
H(8)	0.4201	-0.0219	0.1201	5.1560
H(9)	0.3325	-0.1501	0.2674	9.2473
H(10)	0.1733	-0.1201	0.2752	9.2473
H(11)	0.2061	-0.1713	0.2329	9.2473
H(12)	0.3384	-0.0206	-0.0519	4.8884
H(13)	0.2603	-0.1204	-0.0958	5.2464
H(14)	-0.0077	0.0086	-0.1715	4.6180

Table 1. Atomic coordinates and Biso/Beq (continued)

atom	x	y	z	B_{eq}
H(15)	0.0609	0.1084	-0.1263	4.5206
H(16)	0.1199	-0.1750	-0.1562	6.6664
H(17)	-0.0352	-0.1395	-0.1626	6.6664
H(18)	0.0893	-0.1247	-0.1991	6.6664
H(19)	0.2910	0.2500	0.1169	4.3150
H(20)	0.5613	0.1396	0.2052	5.4281
H(21)	0.6399	0.2500	0.2365	5.9629
H(22)	0.2036	0.2500	-0.0314	4.1210
H(23)	0.3715	0.1392	-0.1424	4.3225
H(24)	0.4190	0.2500	-0.1797	4.5413
H(25)	-0.2969	0.2500	-0.1066	12.3893
H(26)	-0.2389	0.1393	-0.0714	12.4721
H(27)	-0.1215	0.1385	-0.0013	11.0188
H(28)	0.0692	0.2500	0.0392	18.1826
H(29)	-0.0576	0.2075	0.0640	18.1826

$$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha$$

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	0.084(1)	0.039(1)	0.031(1)	-0.005(1)	-0.008(1)	0.0055(10)
N(2)	0.085(2)	0.036(1)	0.028(1)	-0.007(1)	-0.007(1)	0.0014(9)
C(1)	0.057(1)	0.037(1)	0.030(1)	0.000(1)	-0.005(1)	0.002(1)
C(2)	0.064(2)	0.046(2)	0.035(1)	-0.009(1)	0.004(1)	0.005(1)
C(3)	0.059(2)	0.047(2)	0.039(2)	-0.011(1)	-0.004(1)	0.001(1)
C(4)	0.060(2)	0.035(1)	0.029(1)	-0.002(1)	-0.001(1)	0.001(1)
C(5)	0.051(1)	0.041(1)	0.037(1)	-0.001(1)	0.003(1)	0.005(1)
C(6)	0.050(1)	0.040(1)	0.043(2)	-0.005(1)	-0.008(1)	0.004(1)
C(7)	0.061(2)	0.041(2)	0.032(1)	0.001(1)	-0.006(1)	0.005(1)
C(8)	0.070(2)	0.051(2)	0.035(1)	0.005(1)	-0.006(1)	-0.003(1)
C(9)	0.079(2)	0.065(2)	0.032(1)	-0.004(2)	0.003(1)	0.007(1)
C(10)	0.077(2)	0.056(2)	0.044(2)	-0.004(1)	0.001(1)	0.018(1)
C(11)	0.083(2)	0.040(2)	0.053(2)	0.007(1)	0.006(1)	0.008(1)
C(12)	0.075(2)	0.047(2)	0.041(2)	0.008(1)	0.010(1)	0.005(1)
C(13)	0.146(3)	0.077(2)	0.070(2)	-0.012(2)	0.010(2)	0.033(2)
C(14)	0.055(1)	0.036(1)	0.033(1)	-0.004(1)	-0.001(1)	-0.001(1)
C(15)	0.064(2)	0.044(2)	0.047(2)	0.005(1)	-0.016(1)	-0.001(1)
C(16)	0.063(2)	0.038(2)	0.065(2)	0.008(1)	-0.009(1)	-0.008(1)
C(17)	0.050(2)	0.044(2)	0.044(2)	-0.003(1)	0.005(1)	-0.011(1)
C(18)	0.053(2)	0.053(2)	0.040(2)	-0.006(1)	-0.005(1)	0.000(1)
C(19)	0.058(2)	0.040(1)	0.045(2)	0.004(1)	-0.004(1)	0.002(1)
C(20)	0.074(2)	0.062(2)	0.075(2)	-0.009(1)	0.000(2)	-0.021(2)
C(21)	0.058(2)	0.043(2)	0.036(2)	0.0000	-0.012(2)	0.0000
C(22)	0.064(2)	0.042(2)	0.032(1)	-0.002(1)	-0.007(1)	0.001(1)
C(23)	0.072(2)	0.050(2)	0.050(2)	0.004(1)	-0.020(1)	0.004(1)
C(24)	0.073(3)	0.063(3)	0.054(2)	0.0000	-0.029(2)	0.0000
C(25)	0.059(2)	0.044(2)	0.028(2)	0.0000	0.003(2)	0.0000
C(26)	0.057(1)	0.036(1)	0.028(1)	-0.001(1)	-0.004(1)	0.000(1)
C(27)	0.064(2)	0.040(1)	0.033(1)	0.002(1)	0.000(1)	-0.004(1)
C(28)	0.063(2)	0.052(2)	0.029(2)	0.0000	0.007(2)	0.0000
C(29)	0.118(6)	0.162(9)	0.113(7)	0.0000	-0.029(5)	0.0000
C(30)	0.087(4)	0.187(7)	0.120(5)	0.011(4)	0.005(4)	-0.017(5)
C(31)	0.082(3)	0.131(5)	0.135(5)	0.008(3)	0.026(4)	0.007(4)
C(32)	0.070(4)	0.22(1)	0.042(4)	0.0000	-0.006(3)	0.0000
C(33)	0.196(10)	0.19(1)	0.19(1)	0.0000	0.078(9)	0.0000

The general temperature factor expression:

$\exp(-2\pi^2(a^*2U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
N(1)	C(1)	1.426(3)	N(1)	C(7)	1.422(3)
N(1)	C(22)	1.422(3)	N(2)	C(4)	1.416(3)
N(2)	C(14)	1.417(3)	N(2)	C(26)	1.423(3)
C(1)	C(2)	1.384(3)	C(1)	C(6)	1.385(3)
C(2)	C(3)	1.392(3)	C(3)	C(4)	1.390(3)
C(4)	C(5)	1.383(3)	C(5)	C(6)	1.378(3)
C(7)	C(8)	1.391(3)	C(7)	C(12)	1.383(3)
C(8)	C(9)	1.373(3)	C(9)	C(10)	1.378(3)
C(10)	C(11)	1.381(3)	C(10)	C(13)	1.511(4)
C(11)	C(12)	1.381(3)	C(14)	C(15)	1.382(3)
C(14)	C(19)	1.389(3)	C(15)	C(16)	1.384(3)
C(16)	C(17)	1.377(3)	C(17)	C(18)	1.376(3)
C(17)	C(20)	1.518(3)	C(18)	C(19)	1.380(3)
C(21)	C(22)	1.382(3)	C(21)	C(22)	1.382(3)
C(22)	C(23)	1.390(3)	C(23)	C(24)	1.372(3)
C(25)	C(26)	1.385(3)	C(25)	C(26)	1.385(3)
C(26)	C(27)	1.389(3)	C(27)	C(28)	1.380(3)
C(29)	C(30)	1.376(7)	C(29)	C(30)	1.376(7)
C(30)	C(31)	1.297(8)	C(31)	C(32)	1.397(6)
C(32)	C(33)	1.35(1)			

Table 5. Bond Angles(^{o})

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	N(1)	C(7)	120.3(2)	C(1)	N(1)	C(22)	119.3(2)
C(7)	N(1)	C(22)	120.4(2)	C(4)	N(2)	C(14)	121.7(2)
C(4)	N(2)	C(26)	118.3(2)	C(14)	N(2)	C(26)	119.7(2)
N(1)	C(1)	C(2)	121.4(2)	N(1)	C(1)	C(6)	120.5(2)
C(2)	C(1)	C(6)	118.1(2)	C(1)	C(2)	C(3)	120.7(2)
C(2)	C(3)	C(4)	120.9(2)	N(2)	C(4)	C(3)	121.3(2)
N(2)	C(4)	C(5)	120.8(2)	C(3)	C(4)	C(5)	117.9(2)
C(4)	C(5)	C(6)	121.1(2)	C(1)	C(6)	C(5)	121.3(2)
N(1)	C(7)	C(8)	120.8(2)	N(1)	C(7)	C(12)	121.1(2)
C(8)	C(7)	C(12)	118.1(2)	C(7)	C(8)	C(9)	120.7(2)
C(8)	C(9)	C(10)	121.7(2)	C(9)	C(10)	C(11)	117.2(2)
C(9)	C(10)	C(13)	121.2(3)	C(11)	C(10)	C(13)	121.6(3)
C(10)	C(11)	C(12)	122.0(2)	C(7)	C(12)	C(11)	120.2(2)
N(2)	C(14)	C(15)	121.5(2)	N(2)	C(14)	C(19)	120.4(2)
C(15)	C(14)	C(19)	118.1(2)	C(14)	C(15)	C(16)	120.2(2)
C(15)	C(16)	C(17)	122.2(2)	C(16)	C(17)	C(18)	117.2(2)
C(16)	C(17)	C(20)	121.3(2)	C(18)	C(17)	C(20)	121.4(2)
C(17)	C(18)	C(19)	121.7(2)	C(14)	C(19)	C(18)	120.6(2)
C(22)	C(21)	C(22)	121.6(3)	N(1)	C(22)	C(21)	120.1(2)
N(1)	C(22)	C(23)	121.0(2)	C(21)	C(22)	C(23)	118.8(2)
C(22)	C(23)	C(24)	119.5(2)	C(23)	C(24)	C(23)	121.7(3)
C(26)	C(25)	C(26)	121.4(3)	N(2)	C(26)	C(25)	120.1(2)
N(2)	C(26)	C(27)	120.7(2)	C(25)	C(26)	C(27)	119.2(2)
C(26)	C(27)	C(28)	119.3(2)	C(27)	C(28)	C(27)	121.6(3)
C(30)	C(29)	C(30)	122.3(9)	C(29)	C(30)	C(31)	119.2(7)
C(30)	C(31)	C(32)	119.4(6)	C(31)	C(32)	C(31)	120.5(7)
C(31)	C(32)	C(33)	119.6(4)	C(31)	C(32)	C(33)	119.6(4)

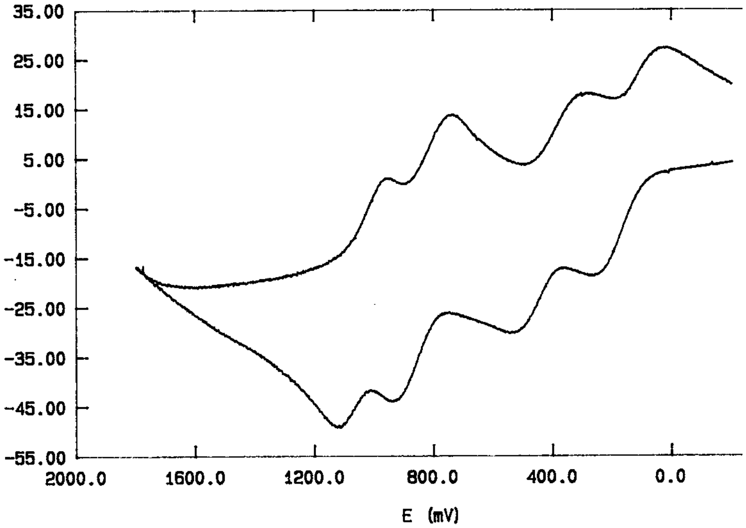
Table 6. Bond Angles(°) for the Hydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	C(2)	H(1)	119.7	C(3)	C(2)	H(1)	119.7
C(2)	C(3)	H(2)	119.6	C(4)	C(3)	H(2)	119.6
C(4)	C(5)	H(3)	119.4	C(6)	C(5)	H(3)	119.4
C(1)	C(6)	H(4)	119.4	C(5)	C(6)	H(4)	119.4
C(7)	C(8)	H(5)	119.6	C(9)	C(8)	H(5)	119.6
C(8)	C(9)	H(6)	119.1	C(10)	C(9)	H(6)	119.1
C(10)	C(11)	H(7)	119.0	C(12)	C(11)	H(7)	119.0
C(7)	C(12)	H(8)	119.9	C(11)	C(12)	H(8)	119.9
C(10)	C(13)	H(9)	109.5	C(10)	C(13)	H(10)	109.5
C(10)	C(13)	H(11)	109.5	H(9)	C(13)	H(10)	109.5
H(9)	C(13)	H(11)	109.5	H(10)	C(13)	H(11)	109.5
C(14)	C(15)	H(12)	119.9	C(16)	C(15)	H(12)	119.9
C(15)	C(16)	H(13)	118.9	C(17)	C(16)	H(13)	118.9
C(17)	C(18)	H(14)	119.1	C(19)	C(18)	H(14)	119.1
C(14)	C(19)	H(15)	119.7	C(18)	C(19)	H(15)	119.7
C(17)	C(20)	H(16)	109.5	C(17)	C(20)	H(17)	109.5
C(17)	C(20)	H(18)	109.5	H(16)	C(20)	H(17)	109.5
H(16)	C(20)	H(18)	109.5	H(17)	C(20)	H(18)	109.5
C(22)	C(21)	H(19)	119.2	C(22)	C(21)	H(19)	119.2
C(22)	C(23)	H(20)	120.3	C(24)	C(23)	H(20)	120.3
C(23)	C(24)	H(21)	119.2	C(23)	C(24)	H(21)	119.2
C(26)	C(25)	H(22)	119.3	C(26)	C(25)	H(22)	119.3
C(26)	C(27)	H(23)	120.3	C(28)	C(27)	H(23)	120.3
C(27)	C(28)	H(24)	119.2	C(27)	C(28)	H(24)	119.2
C(30)	C(29)	H(25)	118.8	C(30)	C(29)	H(25)	118.8
C(29)	C(30)	H(26)	120.4	C(31)	C(30)	H(26)	120.4
C(30)	C(31)	H(27)	120.3	C(32)	C(31)	H(27)	120.3
C(32)	C(33)	H(28)	109.4	C(32)	C(33)	H(29)	109.4
C(32)	C(33)	H(29)	109.4	H(28)	C(33)	H(29)	109.6
H(28)	C(33)	H(29)	109.6	H(29)	C(33)	H(29)	109.5

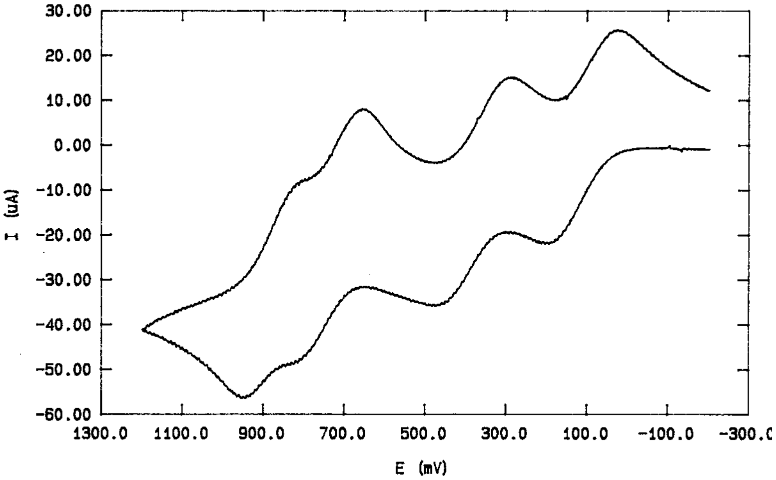
Table 7. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
N(1)	C(1)	C(2)	C(3)	176.8(2)	N(1)	C(1)	C(6)	C(5)	-177.3(2)
N(1)	C(7)	C(8)	C(9)	78.2(2)	N(1)	C(7)	C(12)	C(11)	-177.1(2)
N(1)	C(22)	C(21)	C(22)	-175.6(2)	N(1)	C(22)	C(23)	C(24)	178.7(3)
N(2)	C(4)	C(3)	C(2)	-175.5(2)	N(2)	C(4)	C(5)	C(6)	175.1(2)
N(2)	C(14)	C(15)	C(16)	-178.8(2)	N(2)	C(14)	C(19)	C(18)	177.5(2)
N(2)	C(26)	C(25)	C(26)	176.6(2)	N(2)	C(26)	C(27)	C(28)	-178.6(2)
C(1)	N(1)	C(7)	C(8)	-141.7(2)	C(1)	N(1)	C(7)	C(12)	37.4(3)
C(1)	N(1)	C(22)	C(21)	37.8(4)	C(1)	N(1)	C(22)	C(23)	-141.8(2)
C(1)	C(2)	C(3)	C(4)	0.4(4)	C(1)	C(6)	C(5)	C(4)	0.6(4)
C(2)	C(1)	N(1)	C(7)	38.0(3)	C(2)	C(1)	N(1)	C(22)	-140.8(2)
C(2)	C(1)	C(6)	C(5)	2.0(3)	C(2)	C(3)	C(4)	C(5)	2.1(3)
C(3)	C(2)	C(1)	C(6)	-2.5(3)	C(3)	C(4)	N(2)	C(14)	-44.3(3)
C(3)	C(4)	N(2)	C(26)	141.8(2)	C(3)	C(4)	C(5)	C(6)	-2.6(3)
C(4)	N(2)	C(14)	C(15)	-37.2(3)	C(4)	N(2)	C(14)	C(19)	143.9(2)
C(4)	N(2)	C(26)	C(25)	-41.5(3)	C(4)	N(2)	C(26)	C(27)	137.6(2)
C(5)	C(4)	N(2)	C(14)	138.1(2)	C(5)	C(4)	N(2)	C(26)	-35.9(3)
C(6)	C(1)	N(1)	C(7)	-142.7(2)	C(6)	C(1)	N(1)	C(22)	38.4(3)
C(7)	N(1)	C(22)	C(21)	-141.1(3)	C(7)	N(1)	C(22)	C(23)	39.4(3)
C(7)	C(8)	C(9)	C(10)	-0.5(4)	C(7)	C(12)	C(11)	C(10)	-1.8(4)
C(8)	C(7)	N(1)	C(22)	37.2(3)	C(8)	C(7)	C(12)	C(11)	2.0(4)
C(8)	C(9)	C(10)	C(11)	0.8(4)	C(8)	C(9)	C(10)	C(13)	-178.5(3)
C(9)	C(8)	C(7)	C(12)	-0.9(4)	C(9)	C(10)	C(11)	C(12)	0.3(4)
C(12)	C(7)	N(1)	C(22)	-143.7(2)	C(12)	C(11)	C(10)	C(13)	179.7(3)
C(14)	N(2)	C(26)	C(25)	144.4(2)	C(14)	N(2)	C(26)	C(27)	-36.4(3)
C(14)	C(15)	C(16)	C(17)	1.1(4)	C(14)	C(19)	C(18)	C(17)	1.7(4)
C(15)	C(14)	N(2)	C(26)	136.7(2)	C(15)	C(14)	C(19)	C(18)	-1.5(3)
C(15)	C(16)	C(17)	C(18)	-0.9(4)	C(15)	C(16)	C(17)	C(20)	-179.4(2)
C(16)	C(15)	C(14)	C(19)	0.2(4)	C(16)	C(17)	C(18)	C(19)	-0.5(4)
C(19)	C(14)	N(2)	C(26)	-42.3(3)	C(19)	C(18)	C(17)	C(20)	178.0(2)
C(21)	C(22)	C(23)	C(24)	-0.8(4)	C(21)	C(22)	C(23)	C(24)	0.8(4)
C(22)	C(21)	C(22)	C(23)	-4.0(5)	C(22)	C(23)	C(24)	C(23)	-2.3(6)
C(25)	C(26)	C(27)	C(28)	0.5(4)	C(25)	C(26)	C(27)	C(28)	-0.5(4)
C(26)	C(25)	C(26)	C(27)	2.6(5)	C(26)	C(27)	C(28)	C(27)	1.5(5)
C(29)	C(30)	C(31)	C(32)	0.8(9)	C(29)	C(30)	C(31)	C(32)	-0.8(9)
C(30)	C(29)	C(30)	C(31)	0(1)	C(30)	C(31)	C(32)	C(31)	-1(1)
C(30)	C(31)	C(32)	C(33)	-175.3(6)					

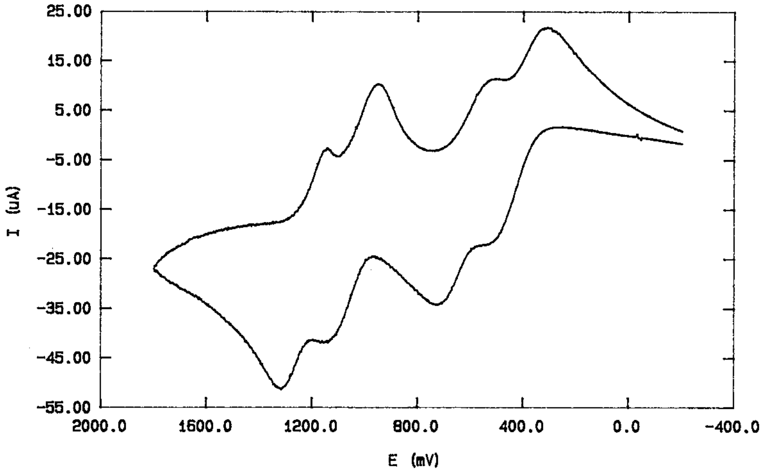
Cycllic Voltametry in CH_2Cl_2



4 in CH_2Cl_2

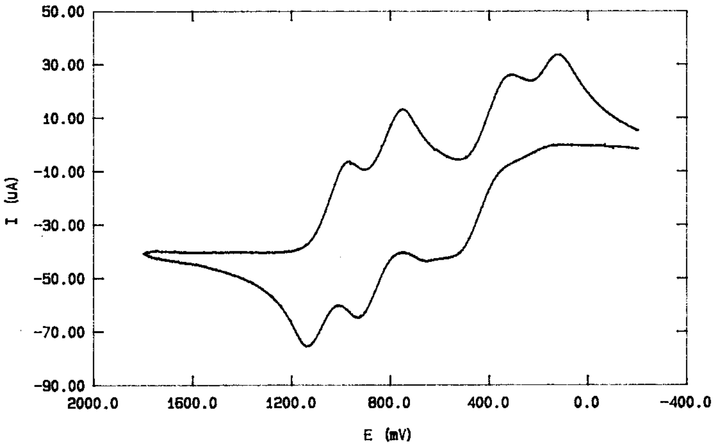


6 in CH_2Cl_2

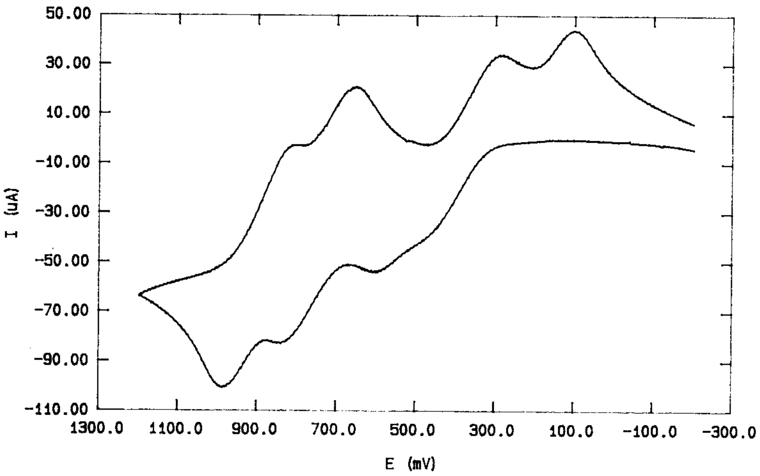


23 in CH_2Cl_2

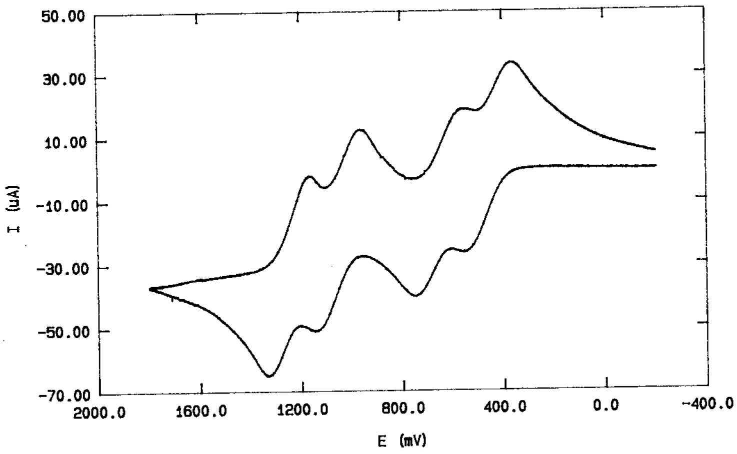
Cyclic Voltametry in CH_2Cl_2/TFA



4 in CH_2Cl_2/TFA

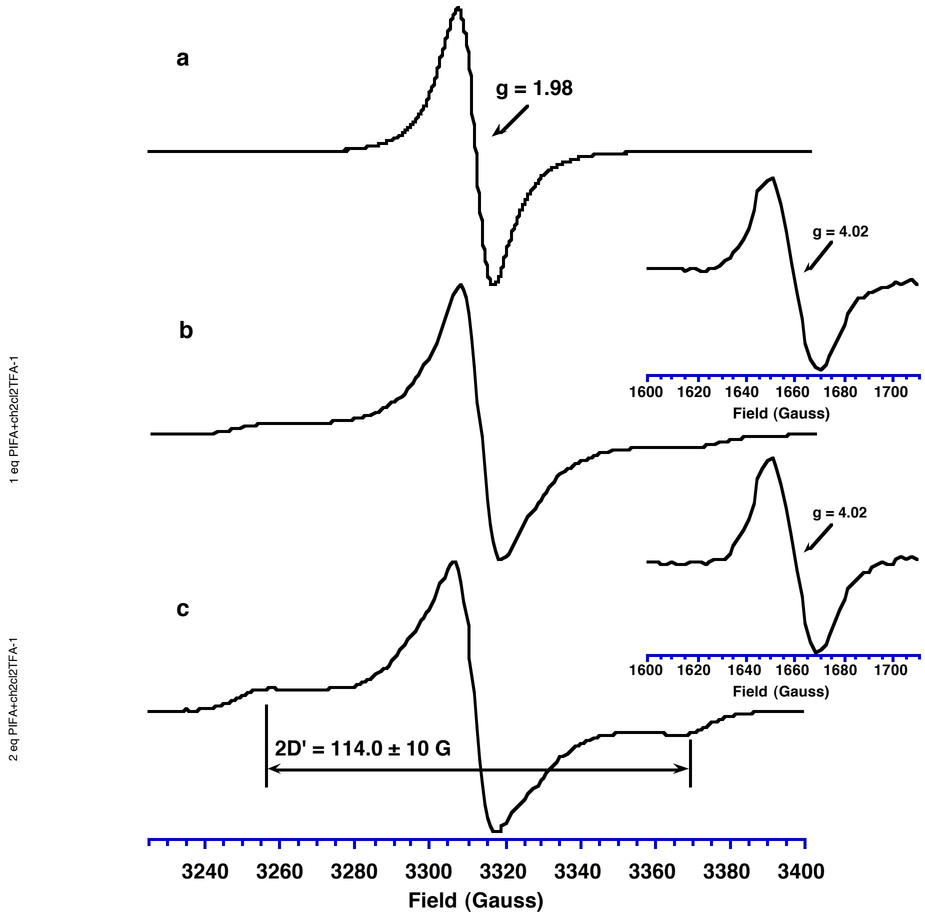


6 in CH_2Cl_2/TFA



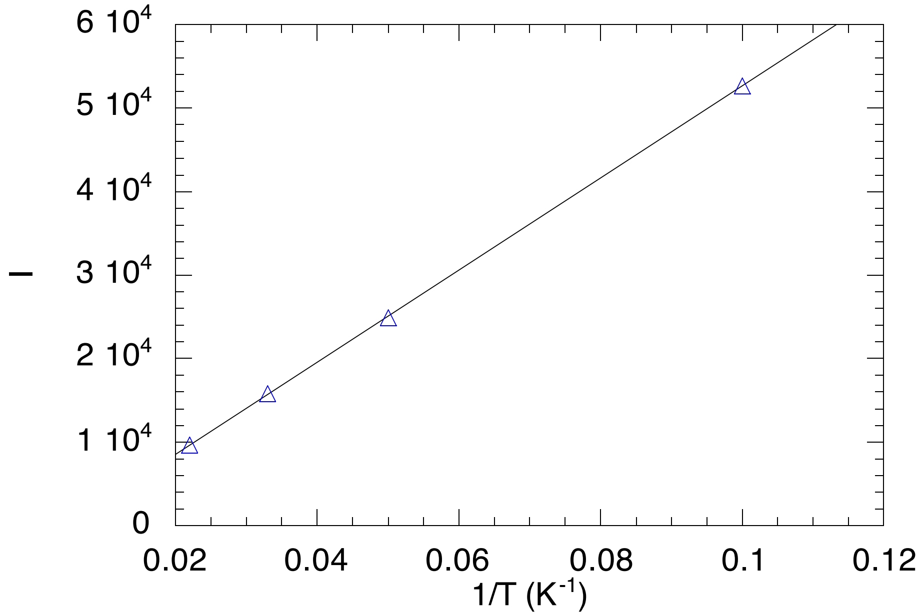
23 in CH_2Cl_2/TFA

EPR of p-methyl cyclophane 4



(a) g = 1.98 EPR signal from the addition of one equiv of PIFA to *p*-methyl cyclophane **4** in CH_2Cl_2**.** **(b-c)** A split EPR signal at g = 1.98 (with peak separations of 2D' = 114 ± 10 G) from the addition of one **(b)** and two **(c)** equiv of bis(trifluoroacetoxy)iodobenzene and 1 % by volume trifluoroacetic acid to **4** in CH_2Cl_2. Shown as insets are the corresponding $\Delta M_S = 2$ half-field transition observed at g = 4.02.

Spectral measurements were conducted at 20 K, and typically 1-2 transients were averaged for each of the spectra shown. Instrumental parameters were as follows:
For a: microwave frequency = 9.28 GHz; microwave power = 0.03 mW; modulation frequency = 100 kHz; modulation amplitude = 4.0 G.
For b-c: (i) g = 1.98 signal: microwave frequency = 9.28 GHz; microwave power = 0.02 mW; modulation frequency = 100 kHz; modulation amplitude = 4.0 G.
(ii) g = 4.02 signal: microwave frequency = 9.28 GHz; microwave power = 20 mW; modulation frequency = 100 kHz; modulation amplitude = 20.0 G.



Curie plot of the intensity of the g = 4 signal vs 1/T for cyclophane **6**