Supporting Information for

Macrocyclic Poly Arylamines for Rigid Connection of Poly Radical Cation Spins

Trent D. Selby and Silas C. Blackstock*

Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336

General Methods and Materials. All reactions were performed under a dry nitrogen atmosphere. Copper powder (99%, "for organic synthesis"), diphenylether, 2,7-dihydroxynaphthalene, 4-anisidine and 1,4-diiodobenzene were purchased from Aldrich Chemical Co. and used without further purification. Thin layer chromatography was performed on Selecto Scientific precoated silica gel F-254 (200 micron) or basic alumina F-254 (200 micron) plates. Column chromatography was performed on silica gel (J.T. Baker, 40 μm flash) or basic alumina (Aldrich, activated Brockmann I, ~150 mesh). Activity III basic alumina was prepared with 6% H_2O.

Infrared spectra were recorded on a Nicolet 360 FT-IR. Nuclear magnetic resonance spectra were recorded on Bruker AM360 or AM500 spectrometers. Chemical shifts are reported (δ) in ppm relative to TMS for proton spectra and relative to the solvent signal for carbon spectra. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA.

Cyclic voltammetry (CV) was performed on a PAR 273 potentiostat (EG&G Instruments). A four-necked CV cell (10 mL) equipped with a Pt disc (1.6 mm diameter) working electrode, a Pt wire counter electrode, and a saturated calomel electrode (SCE) reference was used for routine CV measurements which were carried out under an inert atmosphere. Tetrabutylammonium tetrafluoroborate (Aldrich) was used as supporting electrolyte (0.1M solution) for

electrochemical experiments. A capacitor (0.1 μF), connected between the reference electrode and counter electrode, was used to reduce background noise.

ESR Spectroscopy. X-band ESR spectra were recorded on a Varian E-3 spectrometer. All glassware was flame dried prior to use and allowed to cool under a dry nitrogen atmosphere. Solvents used in ESR measurements were purified by standard methods[1] and deaerated with nitrogen purge or freeze-pump-thaw degassed prior to use. ESR samples of the radical cations were prepared by mixing neutrals **3** or **4** with stoichiometric amounts of thianthrenium perchlorate[2] in CH_2Cl_2 or $CH_3CH_2CH_2CN$.

N,N′-Bis(4-methoxyphenyl)-N,N′-bis(4-iodophenyl)-2,7-naphthalenediamine. 5 (2.60 g, 7.02 mmol), 1,4-diiodobenzene (115.8 g, 0.3510 mol), Cu powder (0.90 g, 14 mmol), anhydrous K_2CO_3 (1.96 g, 14.2 mmol), and diphenylether (15 mL) were heated together at 190 C for 36 hours with stirring. The majority of the diphenylether and excess 1,4-diiodobenzene was then removed by vacuum distillation. The remaining mixture was loaded onto a column of silica gel. Elution with ethyl acetate/hexanes (1:9) afforded 2.44 g (45%) of the desired *p*-diiodo product: mp 156-158 °C. ^{1}H NMR (360 MHz, $CDCl_3$) 7.58 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.8 Hz, 4H), 7.10-7.05 (m, 8H), 6.84 (d, J = 8.8 Hz, 4H), 6.80 (d, J = 8.8 Hz, 4H), 3.80 (s, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) 156.62, 147.84, 145.71, 139.98, 137.94, 135.40, 128.51, 127.55, 126.19, 124.58, 122.03, 118.28, 114.93, 84.21, 55.46. IR (KBr, cm^{-1}) 2955 (w), 2930 (w), 2832 (w), 1624 (m), 1505 (s), 1482 (s), 1262 (s), 1242 (s), 1034 (m), 818 (m). Anal. Calcd. for $C_{36}H_{28}I_2N_2O_2$: C, 55.83; H, 3.64; N, 3.62. Found: C, 55.92; H, 3.67; N, 3.55.

N,N′-Bis(4-methoxyphenyl)-N,N′-bis(3-iodophenyl)-2,7-naphthalenediamine. **5** (2.53 g, 6.83 mmol), 1,3-diiodobenzene (45.0 g, 0.136 mol), Cu powder (1.74 g, 27.3 mmol), anhydrous K_2CO_3 (3.78 g, 27.3 mmol), and diphenylether (10 mL) were heated together at 190 C for 48 hours with stirring. The majority of the diphenylether and excess 1,3-diiodobenzene was then removed by vacuum distillation. The remaining mixture was taken up in benzene, filtered, and absorbed onto silica gel. Elution with ethyl acetate/hexanes (1:9) afforded 2.88 g (54%) of the desired *m*-diiodo product: mp 158-160 °C. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.60 (d, J = 8.7 Hz, 2H), 7.36 (t, J = Hz, 2H), 7.25 (d, J = 7.4 Hz, 2H), 7.12-7.05 (m, 8H), 6.99 (m, 2H), 6.91 (d, J = 7.9 Hz, 2H), 6.87-6.83 (m, 4H), 3.80 (s, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) 156.67, 149.39, 145.68, 139.93, 135.42, 131.05, 130.67, 130.47, 128.58, 127.62, 126.35, 122.19, 121.76, 118.68, 114.97, 94.55, 55.46. IR (KBr, cm^{-1}) 2950 (w), 2925 (w), 1625 (m), 1578 (s), 1505 (s), 1470 (s), 1271 (m), 1242 (s), 1035 (m), 829 (m). Anal. Calcd. for $C_{36}H_{28}I_2N_2O_2$: C, 55.83; H, 3.64; N, 3.62. Found: C, 55.60; H, 3.49; N, 3.54.

Macrocycle 3. N,N′-Bis(4-methoxyphenyl)-N,N′-bis(4-iodophenyl)-2,7-naphthalene-diamine (2.75 g, 3.55 mmol), **5** (1.31 g, 3.55 mmol), Cu powder (1.00 g, 15.7 mmol), anhydrous K_2CO_3 (0.98 g, 7.1 mmol), and diphenylether (150 mL) were heated together at 190 °C for 48 hours with stirring. The diphenylether was then removed by vacuum distillation. The remaining mixture was taken up in benzene, filtered and loaded onto a column of basic alumina (activity III). Elution with benzene afforded **3**, 0.88 g (28%): mp 250 °C. ^{1}H NMR (360 MHz, $CDCl_3$) 7.51 (d, J = 8.9 Hz, 4H), 7.13 (d, J = 8.9 Hz, 8H), 7.05 (s, 8H), 7.02 (d, J = 2.0 Hz, 4H), 6.85-6.82 (m, 12H), 3.80 (s, 12H); ^{13}C NMR (90 MHz, $CDCl_3$) 156.00, 147.39, 143.83, 140.38, 135.31, 127.96, 127.09, 126.49, 124.35, 119.91, 114.81, 114.58, 55.47. IR (KBr, cm^{-1}) 3032 (w), 2925 (w), 2827

(w), 1627 (s), 1503 (s), 1461 (m), 1242 (s), 1036 (m), 828 (m). Anal. Calcd. for $C_{60}H_{48}N_4O_4$: C, 81.06; H, 5.44; N, 6.30. Found: C, 81.00; H, 5.41; N, 6.14.

Macrocycle 4. N,N′-Bis(4-methoxyphenyl)-N,N′-bis(3-iodophenyl)-2,7-naphthalene-diamine (2.60 g, 3.36 mmol), **5** (1.24 g, 3.36 mmol), Cu powder (0.860 g, 13.5 mmol), anhydrous K_2CO_3 (1.86 g, 13.5 mmol), and diphenylether (150 mL) were heated together at 190 °C for 48 hours with stirring. The diphenylether was then removed by vacuum distillation. The remaining mixture was taken up in benzene, filtered and loaded onto a column of basic alumina (activity III). Elution with benzene afforded **4**, 0.63 g (21%): mp 273-275 °C. ^{1}H NMR (500 MHz, $CDCl_3$) 7.44 (d, J = 8.7 Hz, 4H), 7.18 (d, J = 2.2 Hz, 2H), 7.15 (t, J = 8.6 Hz, 2H), 7.06-7.04 (m, 12H), 6.91 (dd, J= 8.7, 2.1 Hz, 4H), 6.81 (d, J = 8.8 Hz, 8H), 6.66 (dd, J = 8.6, 2.2 Hz, 4H), 3.79 (s, 12H); ^{13}C NMR (90 MHz, $CDCl_3$) 156.01, 149.10, 146.56, 140.81, 135.63, 130.40, 128.27, 126.91, 125.09, 122.46, 120.95, 120.19, 115.99, 114.53, 55.44. IR (KBr, cm^{-1}) 2945 (w), 2827 (w), 1624 (m), 1587 (m), 1504 (s), 1481 (m), 1461 (m), 1264 (m), 1237 (s), 1160 (m), 1034 (m), 835 (m). Anal. Calcd. for $C_{60}H_{48}N_4O_4$: C, 81.06; H, 5.44; N, 6.30. Found: C, 81.11; H, 5.22; N, 6.17.

N,N′-Bis(4-methoxyphenyl)-2,7-naphthalenediamine (5). **5** was prepared in 86% yield as previously reported.[3]

NMR Magnetic Susceptibility Measurements.

Solution magnetic susceptibility measurements were made by the Evans[4] NMR shift method. Spectra were recorded on a 360.136 MHz NMR spectrometer in $CDCl_3$ for $\mathbf{3}^+$ and $\mathbf{3}^{2+}$

(generated in-situ by oxidation with $TH^+ClO_4^-$). The shifts of the TMS signal and μ_{eff} values are given in Table **1**. For a complete description of the μ_{eff} measurements and calculations see the supporting information of our previous work.[5]

Table 1. NMR-derived Susceptibility Data for the cations of **3** at 301 K.

Substrate	Shift (Hz) of the TMS peak				x_m	μeff
	10mM	20mM	30mM	40mM	x 10^{-3}	
$\mathbf{3}^+$	18.83	38.15	57.47	75.68	1.26	1.74±0.01
$\mathbf{3}^{2+}$	27.50	59.10	88.77	118.09	1.97	2.18±0.04

X-ray Crystallography.

X-ray diffraction analysis was performed on a Siemens SMART diffractometer with CCD area detection at 173 K. Hydrogens were placed in calculated positions. Least squares refinement was performed on F^2. Disordered nitrobenzene (about an inversion center as shown below) was found in the crystal lattice and its poor resolution contributed to a high R-value for this structure. Nevertheless, the macrocyclic ring structure is clearly defined in the lattice. Tables 2 - 4 provide crystal data and structure results for macrocycle **3**.

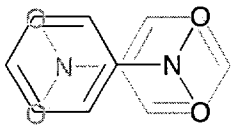

Table 2. Crystal data and structure refinement for macrocycle 3.

Empirical formula	C60 H98 N4 O4 - C6 H5 N O2
Formula weight	939.42
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a=18.140(4) A alpha=90
	b=11.780(2) A beta=107.45(3)
	c=23.678(5) A gamma=90
Volume, Z	4827(2) A^3, 4
Density (calculated)	1.293 Mg/m^3
Absorption coefficient	0.080 mm^-1
F(000)	2072
Theta range for data collection	1.25 to 21.00 deg.
Limiting indices	-16<=h<=21, -13<=k<=12, -27<=l<=23
Reflections collected	16218
Independent reflections	5171 [R(int) = 0.1708]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5021 / 0 / 638
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.1032, wR2 = 0.2260
R indices (all data)	R1 = 0.2267, wR2 = 0.3317
Extinction coefficient	0.0005(3)
Largest diff. peak and hole	0.861 and -0.427 e.A^-3

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(4)	7053(4)	9607(6)	1871(3)	40(2)
N(4)	6409(5)	7374(8)	3756(3)	31(2)
O(3)	4744(4)	9434(6)	9272(3)	35(2)
N(3)	8541(4)	7019(7)	6072(3)	23(2)
N(2)	3174(5)	7105(8)	5036(4)	34(2)
C(60)	4234(6)	7188(9)	4615(4)	26(3)
N(1)	5294(5)	7132(7)	7359(4)	30(2)
C(59)	7134(6)	6797(9)	6960(4)	30(3)
O(2)	99(4)	8294(6)	4770(3)	37(2)
C(58)	4557(6)	7033(8)	4144(4)	21(3)
C(57)	5642(6)	8551(8)	8153(4)	22(3)
C(56)	4064(6)	6632(8)	3585(4)	25(3)
C(55)	8044(5)	7111(9)	5477(4)	22(3)
C(54)	5331(6)	7285(9)	4182(4)	31(3)
C(53)	7395(6)	8153(9)	2637(4)	29(3)
C(52)	7609(6)	6302(9)	7489(4)	29(3)
C(51)	7438(6)	7047(9)	6489(5)	34(3)
C(50)	5626(6)	7159(9)	3714(4)	27(3)
C(49)	6558(6)	6359(9)	7913(4)	30(3)
C(48)	4148(6)	7965(9)	6603(5)	32(3)
C(47)	4365(6)	6498(9)	3101(4)	31(3)
O(1)	11305(4)	9500(6)	6781(3)	44(2)
C(46)	6988(6)	7309(9)	4319(4)	26(3)
C(45)	3678(6)	7115(10)	5636(4)	31(3)
C(44)	8058(6)	8042(9)	5125(4)	29(3)

C(43)	4843(6)	8853(9)	8794(4)	29(3)
C(42)	6369(6)	7117(9)	6933(4)	30(3)
C(41)	4229(6)	6259(9)	5829(5)	35(3)
C(40)	7227(6)	7618(10)	3110(5)	34(3)
C(39)	4500(6)	7475(9)	8017(4)	25(3)
C(38)	2991(6)	6564(9)	4010(5)	38(3)
C(37)	6592(6)	7950(9)	3279(4)	32(3)
C(36)	7019(6)	6322(9)	4668(4)	30(3)
C(35)	3626(6)	7961(9)	6039(4)	31(3)
C(34)	6065(6)	6866(9)	7390(4)	28(3)
C(33)	8677(6)	6286(9)	7056(4)	30(3)
C(32)	5501(6)	9102(8)	8629(4)	24(3)
C(31)	7527(6)	6245(9)	5239(4)	27(3)
C(30)	4333(6)	8025(9)	8489(4)	28(3)
C(29)	6271(6)	9351(9)	2490(5)	29(3)
C(28)	8191(6)	6806(8)	6534(4)	22(3)
C(27)	8393(6)	6026(9)	7523(4)	33(3)
C(26)	6926(6)	9033(9)	2337(4)	29(3)
C(25)	5138(6)	7729(9)	7840(4)	23(3)
C(24)	4742(6)	6259(9)	6396(4)	24(3)
C(23)	4712(6)	7133(9)	6791(4)	24(3)
C(22)	4086(6)	9129(10)	9469(4)	38(3)
C(21)	6119(6)	8838(10)	2970(5)	36(3)
C(20)	2397(6)	7428(10)	4952(4)	30(3)
C(19)	9999(6)	9246(9)	6737(4)	30(3)
C(17)	9254(6)	7641(9)	6250(4)	28(3)
C(16)	5127(7)	6742(9)	3172(4)	32(3)
C(15)	3473(6)	6985(10)	4555(5)	35(3)
C(14)	3269(6)	6385(9)	3535(4)	32(3)

C(13)	7793(6)	9454(10)	1769(5)	43(3)
C(12)	10607(7)	7807(10)	6312(4)	33(3)
C(11)	9307(6)	8652(9)	6564(4)	28(3)
C(10)	1300(6)	8696(9)	4534(4)	29(3)
C(9)	7539(6)	8146(9)	4555(4)	30(3)
C(8)	2065(7)	8367(10)	4620(5)	37(3)
C(7)	868(6)	8086(10)	4800(5)	29(3)
C(6)	1156(6)	7094(9)	5122(4)	30(3)
C(5)	10641(6)	8817(10)	6614(5)	36(3)
C(4)	1909(6)	6786(9)	5191(4)	32(3)
C(3)	-271(7)	9190(10)	4378(5)	45(3)
C(2)	11915(6)	9194(10)	6537(5)	47(3)
C(1)	9906(6)	7228(9)	6125(4)	29(3)
C(18)	7293(6)	6063(9)	7959(4)	28(3)

Table 4. Bond lengths [A] and angles [deg] for 3.

O(4)-C(26)	1.372(11)
O(4)-C(13)	1.444(11)
N(4)-C(50)	1.418(12)
N(4)-C(46)	1.432(12)
N(4)-C(37)	1.438(12)
O(3)-C(43)	1.381(12)
O(3)-C(22)	1.450(12)
N(3)-C(55)	1.432(12)
N(3)-C(17)	1.435(12)
N(3)-C(28)	1.442(12)
N(2)-C(15)	1.408(13)
N(2)-C(20)	1.416(12)
N(2)-C(45)	1.440(12)
C(60)-C(15)	1.366(13)
C(60)-C(58)	1.418(13)
N(1)-C(34)	1.413(13)
N(1)-C(25)	1.437(12)
N(1)-C(23)	1.441(12)
C(59)-C(51)	1.415(14)
C(59)-C(52)	1.416(14)
C(59)-C(42)	1.422(14)
O(2)-C(7)	1.397(12)
O(2)-C(3)	1.432(12)
C(58)-C(54)	1.412(13)
C(58)-C(56)	1.438(13)
C(57)-C(25)	1.384(13)
C(57)-C(32)	1.391(13)
C(56)-C(47)	1.418(13)

C(56)-C(14)	1.442(14)
C(55)-C(44)	1.382(13)
C(55)-C(31)	1.386(13)
C(54)-C(50)	1.376(13)
C(53)-C(40)	1.395(13)
C(53)-C(26)	1.394(14)
C(52)-C(18)	1.426(13)
C(52)-C(27)	1.437(14)
C(51)-C(28)	1.366(13)
C(50)-C(16)	1.417(13)
C(49)-C(18)	1.351(13)
C(49)-C(34)	1.423(13)
C(48)-C(35)	1.386(13)
C(48)-C(23)	1.389(14)
C(47)-C(16)	1.372(14)
O(1)-C(5)	1.402(12)
O(1)-C(2)	1.440(12)
C(46)-C(9)	1.396(14)
C(46)-C(36)	1.418(13)
C(45)-C(41)	1.397(14)
C(45)-C(35)	1.402(14)
C(44)-C(9)	1.400(13)
C(43)-C(30)	1.388(14)
C(43)-C(32)	1.393(13)
C(42)-C(34)	1.386(13)
C(41)-C(24)	1.385(13)
C(40)-C(37)	1.385(14)
C(39)-C(25)	1.377(13)
C(39)-C(30)	1.401(13)

C(38)-C(14)	1.379(14)
C(38)-C(15)	1.414(14)
C(37)-C(21)	1.411(14)
C(36)-C(31)	1.390(13)
C(33)-C(27)	1.385(13)
C(33)-C(28)	1.424(13)
C(29)-C(21)	1.386(14)
C(29)-C(26)	1.392(13)
C(24)-C(23)	1.403(13)
C(20)-C(8)	1.387(14)
C(20)-C(4)	1.406(14)
C(19)-C(5)	1.379(14)
C(19)-C(11)	1.387(14)
C(17)-C(11)	1.391(13)
C(17)-C(1)	1.392(14)
C(12)-C(5)	1.381(14)
C(12)-C(1)	1.393(14)
C(10)-C(7)	1.350(14)
C(10)-C(8)	1.395(14)
C(7)-C(6)	1.408(14)
C(6)-C(4)	1.374(14)

C. J. Burrows

angles

C(26)-O(4)-C(13)	117.5(8)
C(50)-N(4)-C(46)	119.7(8)
C(50)-N(4)-C(37)	119.4(8)
C(46)-N(4)-C(37)	118.7(9)
C(43)-O(3)-C(22)	117.6(8)

C(55)-N(3)-C(17)	119.7(8)
C(55)-N(3)-C(28)	118.0(8)
C(17)-N(3)-C(28)	115.4(8)
C(15)-N(2)-C(20)	121.4(8)
C(15)-N(2)-C(45)	121.0(9)
C(20)-N(2)-C(45)	116.5(9)
C(15)-C(60)-C(58)	122.6(9)
C(34)-N(1)-C(25)	119.6(8)
C(34)-N(1)-C(23)	119.1(8)
C(25)-N(1)-C(23)	118.5(8)
C(51)-C(59)-C(52)	120.3(10)
C(51)-C(59)-C(42)	121.0(9)
C(52)-C(59)-C(42)	118.4(10)
C(7)-O(2)-C(3)	115.4(9)
C(54)-C(58)-C(60)	124.1(9)
C(54)-C(58)-C(56)	117.3(9)
C(60)-C(58)-C(56)	118.5(9)
C(25)-C(57)-C(32)	120.5(9)
C(47)-C(56)-C(58)	119.9(10)
C(47)-C(56)-C(14)	122.0(9)
C(58)-C(56)-C(14)	118.1(9)
C(44)-C(55)-C(31)	118.1(9)
C(44)-C(55)-N(3)	122.2(9)
C(31)-C(55)-N(3)	119.6(9)
C(50)-C(54)-C(58)	123.0(9)
C(40)-C(53)-C(26)	119.9(10)
C(59)-C(52)-C(18)	119.5(10)
C(59)-C(52)-C(27)	118.1(9)
C(18)-C(52)-C(27)	122.4(10)

C(28)-C(51)-C(59)	120.7(10)
C(54)-C(50)-C(16)	118.1(10)
C(54)-C(50)-N(4)	123.2(9)
C(16)-C(50)-N(4)	118.6(9)
C(18)-C(49)-C(34)	121.8(10)
C(35)-C(48)-C(23)	122.1(10)
C(16)-C(47)-C(56)	119.7(9)
C(5)-O(1)-C(2)	116.1(9)
C(9)-C(46)-C(36)	116.6(9)
C(9)-C(46)-N(4)	124.9(10)
C(36)-C(46)-N(4)	118.5(9)
C(41)-C(45)-C(35)	118.6(10)
C(41)-C(45)-N(2)	119.8(10)
C(35)-C(45)-N(2)	121.6(10)
C(55)-C(44)-C(9)	121.5(10)
O(3)-C(43)-C(30)	123.0(10)
O(3)-C(43)-C(32)	117.3(9)
C(30)-C(43)-C(32)	119.7(10)
C(34)-C(42)-C(59)	121.3(9)
C(24)-C(41)-C(45)	121.6(10)
C(37)-C(40)-C(53)	120.4(10)
C(25)-C(39)-C(30)	123.0(10)
C(14)-C(38)-C(15)	121.3(10)
C(40)-C(37)-C(21)	119.3(10)
C(40)-C(37)-N(4)	120.1(10)
C(21)-C(37)-N(4)	120.6(10)
C(31)-C(36)-C(46)	121.2(10)
C(48)-C(35)-C(45)	119.5(10)
C(42)-C(34)-N(1)	122.1(9)

C(42)-C(34)-C(49)	118.4(10)
N(1)-C(34)-C(49)	119.5(9)
C(27)-C(33)-C(28)	120.3(10)
C(43)-C(32)-C(57)	120.7(10)
C(36)-C(31)-C(55)	121.2(10)
C(43)-C(30)-C(39)	118.0(10)
C(21)-C(29)-C(26)	119.5(10)
C(51)-C(28)-C(33)	120.1(10)
C(51)-C(28)-N(3)	124.1(9)
C(33)-C(28)-N(3)	115.7(9)
C(33)-C(27)-C(52)	120.3(10)
O(4)-C(26)-C(53)	123.5(10)
O(4)-C(26)-C(29)	116.1(10)
C(53)-C(26)-C(29)	120.3(10)
C(39)-C(25)-C(57)	118.0(9)
C(39)-C(25)-N(1)	121.2(9)
C(57)-C(25)-N(1)	120.7(9)
C(41)-C(24)-C(23)	119.8(10)
C(48)-C(23)-C(24)	118.5(9)
C(48)-C(23)-N(1)	124.3(10)
C(24)-C(23)-N(1)	117.2(9)
C(29)-C(21)-C(37)	120.5(10)
C(8)-C(20)-N(2)	122.6(10)
C(8)-C(20)-C(4)	116.0(10)
N(2)-C(20)-C(4)	121.3(10)
C(5)-C(19)-C(11)	120.0(10)
C(11)-C(17)-C(1)	119.0(10)
C(11)-C(17)-N(3)	120.5(10)
C(1)-C(17)-N(3)	120.5(10)

C(47)-C(16)-C(50)	121.9(10)
C(60)-C(15)-N(2)	121.3(9)
C(60)-C(15)-C(38)	119.1(10)
N(2)-C(15)-C(38)	119.4(10)
C(38)-C(14)-C(56)	120.3(10)
C(5)-C(12)-C(1)	118.8(11)
C(19)-C(11)-C(17)	120.2(10)
C(7)-C(10)-C(8)	118.4(10)
C(44)-C(9)-C(46)	121.1(10)
C(20)-C(8)-C(10)	123.2(10)
C(10)-C(7)-O(2)	126.4(10)
C(10)-C(7)-C(6)	121.4(10)
O(2)-C(7)-C(6)	112.1(10)
C(4)-C(6)-C(7)	118.5(10)
C(19)-C(5)-C(12)	121.0(10)
C(19)-C(5)-O(1)	116.0(11)
C(12)-C(5)-O(1)	122.8(11)
C(6)-C(4)-C(20)	122.2(10)
C(17)-C(1)-C(12)	121.0(10)
C(49)-C(18)-C(52)	120.3(10)

---

[1] Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; 4th ed.; Pergamon Press: New York, 1996.

[2] **Caution!** Thianthrenium perchlorate ($TH^+ClO_4^-$) is a shock sensitive explosive solid and should be handled with due care. For preparation and properties see Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

[3] (a) Buu-Hoï, N. P. *J. Chem. Soc.* **1952**, 4346. (b) Selby, T. D.; Blackstock, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 7152 (supporting information).

[4] (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Live, D. H.; Chen, S. I. *Anal. Chem.* **1970**, *42*, 791.

[5] Stickley, K. R.; Selby, T. D.; Blackstock, S. C. *J. Org. Chem.* **1997**, *62*, 448.