(C_3), 42.7 (C_6), 53.8 (C_2), 121.8 (C_{10}), 123.0 (C_5), 124.6 (C_3), 124.9 (C_8), 125.4 (C_{10b} or C_{10c}), 125.4 (C_{10c} or C_{10b}), 125.8 (C_7), 126.4 (C_2), 127.3 (C_4), 127.7 (C_9), 128.6 (C_{5a}), 129.2 (C_{10a}), 129.3 (C_{8a}), 130.2 (C_{3a}), 132.8 (C_1), 138.7 (C_6), 210.2 (CO); MS m/z 326 (M^+), 298, 283, 269, 243, 240.

8b: 69% yield; mp 183–184 °C; IR 1714, 842 cm^{-1}; UV λ_{max} (log ϵ) 349 (4.54), 332 (4.39), 318 (3.99), 279 (4.60), 268 (4.31), 257 (3.94), 244 (4.74), 236 nm (4.53); ^1H NMR δ 1.47 (3 H, t, J = 7.6 Hz, Me), 1.95–2.23 (3 H, m), 2.26–2.57 (3 H, m), 2.69–2.75 (2 H, m, H_6), 3.37 (2 H, q, J = 7.6 Hz), 4.66 (1 H, dd, J = 12.2, 5.6 Hz, benzylic), 7.87 (1 H, d, J = 7.8 Hz, H_7), 7.87 (1 H, d, J = 8.0 Hz, H_2), 7.98 (1 H, d, J = 8.9 Hz, H_4), 7.99 (1 H, d, J = 8.9 Hz, H_5), 8.02 (1 H, d, J = 9.7 Hz, H_{10}), 8.11 (1 H, d, J = 7.8 Hz, H_8), 8.15 (1 H, d, J = 8.0 Hz, H_3), 8.30 (1 H, d, J = 9.7 Hz, H_9); ^{13}C NMR δ 16.1 (Me), 26.0 (C_4 or C_5), 26.5 ($MeCH_2$–), 27.8 (C_5 or C_4), 35.0 (C_3), 42.7 (C_6), 53.8 (C_2), 122.6 (C_{10}), 123.5 (C_9), 124.7 (C_3), 125.2 (C_6), 125.4 (C_{10b} or C_{10c}), 125.5 (C_{10c} or C_{10b}), 125.7 (C_7), 126.3 (C_2), 126.6 (C_4), 127.3 (C_5), 128.0 (C_{8a}), 128.7 (C_{10a}), 129.9 (C_{3a}), 130.7 (C_{5a}), 132.6 (C_1), 138.5 (C_8), 210.2 (CO); MS m/z 326 (M^+), 298, 283, 269, 243, 240.

8c: 55% yield; mp 128–130 °C; IR 1710, 871 cm^{-1}; UV λ_{max} (log ϵ) 350 (4.68), 333 (4.52), 319 (4.13), 281 (4.66), 270 (4.44), 259 (4.17), 249 (4.89), 240 nm (4.69); ^1H NMR δ 1.48 (3 H, t, J = 7.6 Hz, Me), 1.57 (9 H, s), 1.95–2.10 (2 H, m), 2.15–2.22 (1 H, m), 2.27–2.32 (1 H, m), 2.38–2.56 (2 H, m, H_3), 2.68–2.71 (2 H, m, H_6), 3.36 (2 H, q, J = 7.6 Hz), 4.60 (1 H, dd, J = 12.1, 5.8 Hz, H_2), 7.72 (1 H, s, H_2), 7.92 (1 H, d, J = 9.4 Hz, H_{10}), 7.98 (1 H, d, J = 9.4 Hz, H_9), 8.04 (1 H, d, J = 9.3 Hz, H_5), 8.14 (1 H, s, H_8), 8.17 (1 H, s, H_6), 8.24 (1 H, d, J = 9.3 Hz, H_4); ^{13}C NMR δ 15.9 (Me), 25.9 (C_4), 26.7 ($MeCH_2$–), 27.6 (C_5), 31.8 (Me_3), 35.0, 35.0 (C_3), 42.6 (C_6), 53.7 (C_2), 121.8 (C_8), 122.0 (C_6), 122.6 (C_{10}), 123.1 (C_4), 123.5 (C_{10c}), 125.3 (C_{10b}), 126.1 (C_2), 126.6 (C_9), 126.7 (C_5), 127.1 (C_{10a}), 127.4 (C_{3a}), 130.7 (C_{8a}), 130.9 (C_{5a}), 132.5 (C_1), 137.7 (C_3), 148.5 (C_7), 210.0 (CO); MS m/z 382 (M^+), 354.

Cyclodehydration of Ketones 8 and Attempted Dehydrogenation of the Products. (i) Dehydrogenation by DDQ. A mixture of ketone **8a** (206 mg, 0.63 mmol) and PPA (31 g) was heated at 100 °C for 2.5 h. The mixture was then added to crushed ice, and the whole was extracted with benzene. The extract was washed with aq $NaHCO_3$ and water then was passed through a short column of Florisil. After removal of a small amount of benzene by azeotropic distillation, DDQ (0.48 g, 2.1 mmol) was added to the eluate and the solution was refluxed for 1 h under Ar. After the mixture cooled to rt, it was passed through a short column of alumina. The red eluate was concentrated, and the residue was recrystallized from hexane to give 21 mg (12%) of **2**: mp 121–122 °C; IR 1440, 1382, 833 cm^{-1}; UV λ_{max} (log ϵ) 390 (4.36), 368 (4.30), 318 (4.40), 300 (4.52), 278 (4.48), 252 (4.81), 247 (4.73), 242 nm (4.69); MS m/z 304 (M^+), 289, 276.

A small quantity (1.7 mg, 1%) of **9a** was also isolated. **9a**: mp 170–171 °C; IR 1512, 913, 890, 835 cm^{-1}; ^1H NMR δ 5.63 (1 H, dd, J = 11.0, 1.2 Hz, cis), 6.02 (1 H, dd, J = 17.4, 1.2 Hz, trans), 7.36–7.44 (1 H, m, H_8), 7.39–7.46 (1 H, m, H_9), 7.80 (1 H, dd, J = 17.4, 11.0 Hz, –CH=), 7.97–8.00 (1 H, m, H_{10}), 8.06–8.09 (1 H, m, H_7), 8.12 (1 H, d, J = 9.4 Hz, H_1), 8.19 (1 H, d, J = 7.8 Hz, H_{12}), 8.20 (1 H, d, J = 7.6 Hz, H_4), 8.33 (1 H, d, J = 7.8 Hz, H_{11}), 8.34 (1 H, d, J = 7.6 Hz, H_5), 8.34 (1 H, d, J = 9.4 Hz, H_2), 8.51 (1 H, s, H_6); MS m/z 302 (M^+), 289, 276.

Similar treatment of **8b** (136 mg, 0.42 mmol) afforded **3** (9.0 mg, 8%) and **9b** (4.3 mg, 3%). **3**: mp 117–118 °C; IR 1440, 1432, 1401, 837 cm^{-1}; UV λ_{max} (log ϵ) 380 (4.17), 362 (4.18), 317 (4.40), 305 (4.53), 280 (4.38), 252 (4.78), 246 (4.68), 242 nm (4.63); MS m/z 304 (M^+), 289.

9b: mp 142–144 °C; IR 1548, 903, 844 cm^{-1}; ^1H NMR δ 5.73 (1 H, dd, J = 11.0, 1.2 Hz, cis), 6.07 (1 H, dd, J = 17.3, 1.2 Hz, trans), 7.41–7.49 (1 H, m, H_8), 7.43–7.51 (1 H, m, H_9), 7.98 (1 H, dd, J = 17.3, 11.0 Hz, –CH=), 8.01–8.05 (1 H, m, H_{10}), 8.04 (1 H, d, J = 8.9 Hz, H_2), 8.11 (1 H, d, J = 8.9 Hz, H_1), 8.13–8.17 (1 H, m, H_7), 8.23 (1 H, d, J = 7.8 Hz, H_{12}), 8.23 (2 H, s, H_3, H_4), 8.36 (1 H, d, J = 7.8 Hz, H_{11}), 8.93 (1 H, s, H_6); MS m/z 302 (M^+), 289, 276.

(ii) Dehydrogenation by TTFA. A mixture of ketone **8a** (100 mg, 0.31 mmol) and PPA (3.6 g) was heated at 110 °C for 2.5 h. After treatment as described above, a mixture of the crude product (0.1 g), trityl alcohol (0.21 g, 0.81 mmol), and TFA (2 mL) was refluxed for 8.5 h. The mixture was then added to crushed ice, and the whole was extracted with benzene. The extract was dried and concentrated. Triphenylmethane was removed from the solid residue by vacuum sublimation at 100 °C. The residual solid was recrystallized from EtOH to give 5 mg (5%) of **2**, which was identical in all respects with the specimen obtained earlier.

(iii) Dehydrogenation by Pd/C. Ketone **8c** (2.85 g, 7.4 mmol) was treated with PPA (98 g) as described above. A mixture of the crude products, 5% Pd/C (660 mg), and *p*-cymene (15 mL) was refluxed for 155 h. After removal of Pd/C by filtration and *p*-cymene by steam distillation, the residue was purified by column chromatography on silica gel (hexane) to give 1.28 g (48%) of **10**: mp 148–150 °C; IR 1443, 878, 738 cm^{-1}; UV λ_{max} (log ϵ) 429 (3.78), 388 (3.76), 365 (4.11), 319 (4.22), 305 (4.54), 277 (4.47), 254 nm (4.88); MS m/z 360 (M^+), 345.

Similarly, **8a** (370 mg, 1.13 mmol) gave 137 mg (39%) of **2**, mp 120–122 °C, and **8b** (417 mg, 1.28 mmol) afforded 85 mg (22%) of **3**, mp 116–118 °C.

Hydrocarbon 4. A mixture of 12-acetylindeno[1,2,3-*cd*]pyrene (95 mg, 0.3 mmol), diethylene glycol (55 mL), 95% $N_2H_4 \cdot H_2O$ (1 mL, 19 mmol), and NaOH (135 mg, 3 mmol) was heated at 100 °C for 2 h then at 210 °C for 2 h. Workup gave 55 mg (60%) of **4**: mp 122–124 °C; IR 1447, 1378, 824 cm^{-1}; UV λ_{max} (log ϵ) 413 (3.88), 377 (4.12), 360 (4.15), 317 (4.27), 304 (4.58), 277 (4.38), 251 nm (4.83); MS m/z 304 (M^+), 289, 287, 276.

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Registry No. 1, 193-39-5; 2, 138060-63-6; 3, 138060-64-7; 4, 138060-65-8; 5a, 123348-29-8; 5b, 123348-30-1; 6a, 138060-66-9; 6b, 138060-67-0; 6c, 138060-68-1; 7a, 138060-69-2; 7b, 138060-70-5; 7c, 138060-71-6; 8a, 138060-72-7; 8b, 138060-73-8; 8c, 138060-74-9; 9a, 138060-75-0; 9b, 138060-76-1; 10, 138060-77-2; 1-ethylpyrene, 17088-22-1; 7-*tert*-butyl-1-pyrene, 138060-78-3; cyclohexene oxide, 286-20-4; 12-acetylindeno[1,2,3-*cd*]pyrene, 120362-67-6.

Supplementary Material Available: ^1H NMR spectra of 7-*tert*-butyl-1-ethylpyrene, **2–4**, **6b**, **6c**, and **7–10** (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

A Highly Rigid Capped Porphyrin

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Introduction

Cytochrome c oxidase is a polymetallic enzyme which is responsible for dioxygen reduction at the end of the mitochondrial respiratory chain of eukaryotic organisms.[1] The monomeric unit contains four metals, two iron atoms Fe_a and Fe_{a3}, respectively, associated with two copper atoms Cu_A and Cu_B. The catalytic process $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ seems to be a consequence of a cooperative interaction between the heme iron, cyt a_3 and copper, Cu_B, located at a distance of 3 Å according to recent EXAFS

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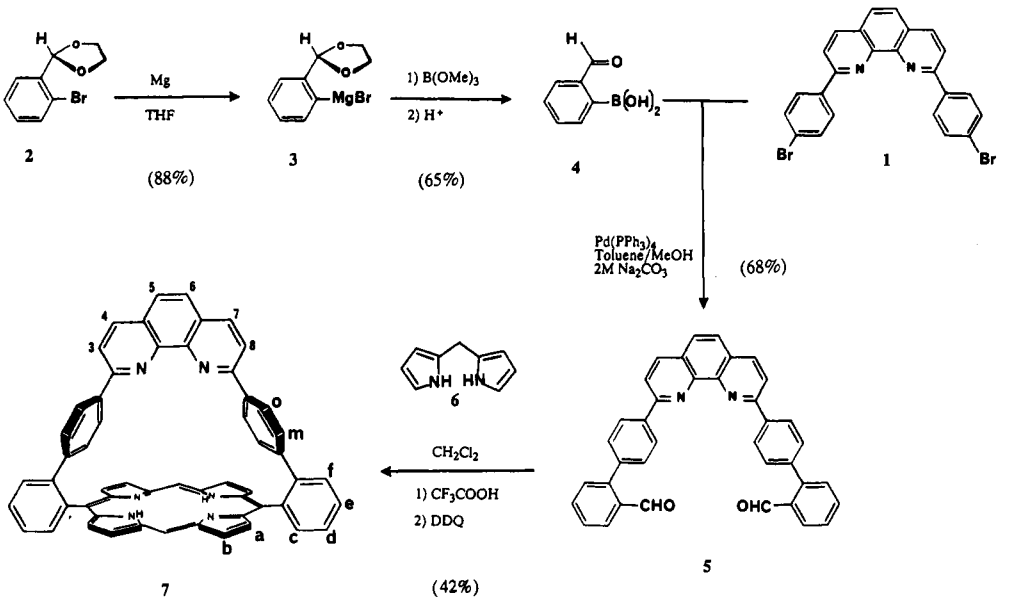

Figure 1. Four-step synthesis of phenanthroline-capped porphyrin **7**.

measurements.[1] This bimetallic complex appears to be the site of O_2 complexation and reduction, while Fe_a and Cu_A supply the electrons required for the process.[2] Different states of the enzyme have been characterized by EPR measurements,[2] UV–vis, or X-ray absorption[1] and Raman resonance.[3] The initial state of the enzyme involves Fe_{a3} as a Fe(II) ion and Cu_B as a Cu(I) ion. Bimetallic species have been used as models for the active site of cytochrome c oxidase and have been obtained following two main approaches. On the one hand, the bimetallic complexes were the result of gathering two mononuclear complexes of iron(III) and copper(II) around bridging ligands such as imidazolate,[4] bipyrimidyls,[5] O^{2-},[6] halogens,[7] and more recently sulfur atoms.[8] On the other hand, a few research

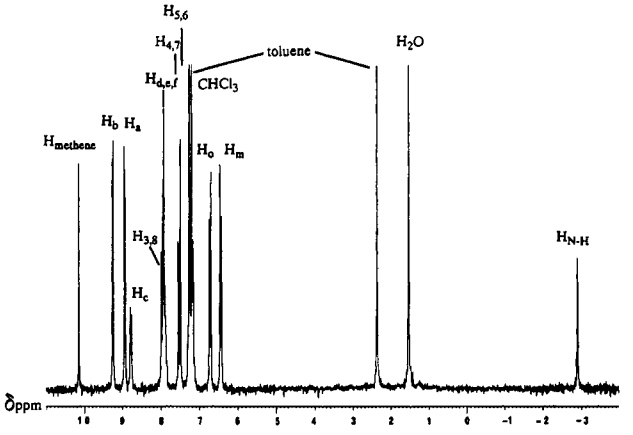

Figure 2. ^1H NMR spectrum of **7**.

groups have succeeded in attaching binding sites for copper(II) ions to porphyrin derivatives,[9] but, although the oxidation state for Cu_B in the initial state is +1, none of the models proposed provides a good binding site for copper(I). Taking advantage of the numerous synthetic methods leading to substituted *meso*-diphenylporphyrins by reacting dipyrrylmethanes with substituted benzaldehydes,[10] we have prepared in few steps a singly strapped porphyrin, containing a phenanthroline as binding site[11] for copper(I) or -(II) and a porphyrin. The molecular architecture is rigid, and the two independent

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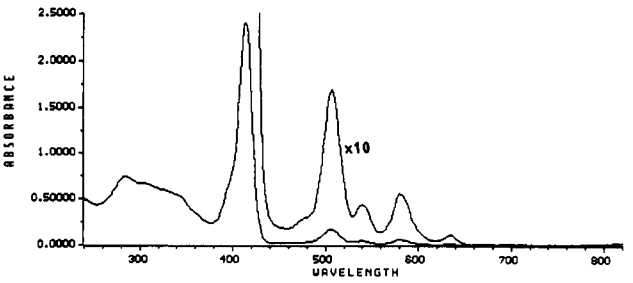

Figure 3. UV–vis spectrum of 7.

coordinating sites are separated by phenyl spacers.

Results

The 2,9-bis(*p*-bromophenyl)-1,10-phenanthroline (1) (Figure 1) was obtained by previously reported methods.[12] On the other hand, treatment of the quantitatively protected[13] *o*-bromobenzaldehyde 2 with magnesium in dry tetrahydrofuran (THF) afforded the Grignard reagent in 97% yield.[14] The quenching of the Grignard with an excess of trimethyl borate, followed by an acidic workup, afforded the deprotected boronic acid 4 in 65% yield as white crystals from CH_2Cl_2. The building blocks 1 and 2 were then reacted under "Suzuki" cross-coupling conditions which have been described by several authors.[15] The reaction in the presence of $Pd(PPh_3)_4$ as catalyst in toluene, aqueous Na_2CO_3, and methanol at 80 °C afforded the dialdehyde 5 in 76% yield.

The dipyrrylmethane unit 6 was prepared according to literature[16] and condensed (Figure 1) with the dialdehyde 5 in a 2:1 ratio in a very dilute CH_2Cl_2 solution containing an excess of trifluoroacetic acid.[17] Dilution considerably enhanced the yields of the cyclization reaction during the course of this work. An in situ oxidation with dichlorodicyanoquinone (DDQ) afforded a dark brown solution. Much cleaner reaction mixtures were obtained when oxidization and extractions were carried out under argon. The deep red porphyrin 7 was isolated in 42% yield, which is remarkable for a macrobicycle formation involving six reaction centers.

The ^1H NMR spectrum (Figure 2) shows clearly the superposition of the diphenyl phenanthroline (dpp) and the *meso*-diphenyl porphyrin (por) spectra. Chemical shift displacements are in agreement with the structure depicted in Figure 2. Compared to a free dpp, the H_o and H_m protons are dramatically shielded, especially H_o for which $\Delta\delta = -2.0$ ppm while for H_m $\Delta\delta = -0.8$ ppm. This clearly shows that the phenyl spacers, included in the dpp unit, are perpendicular to the phenanthroline plan; otherwise, a deshielding effect from the phenanthroline nucleus would have affected H_o. The displacements of the other protons from the dpp $H_{4,7}$, $H_{3,8}$, and $H_{5,6}$ are, respectively, –0.6, –0.6, and –0.3 ppm, which is consistent with their location far above the porphyrin nucleus. In the UV–vis spectrum (Figure 3), the visible region exhibits the Q bands from the porphyrin including, at 412 nm, the very intense Soret band, while the UV region shows a typical phen absorption, confirming the presence of both coordinating sites within the structure of the ligand.

In conclusion, we have developed a rapid synthesis for a highly rigid phenanthroline-capped porphyrin. The two coordination sites maintained within the molecular framework are independent and known for binding numerous transition metals. Of particular interest regarding the design of models for the different states of cytochrome c oxidase, the coordination of iron(III), iron(II), copper(I), and copper(II) is now being investigated.

Experimental Section

All reagents or solvents were used as commercial grades, except THF distilled from $LiAlH_4$ under argon. Melting points are uncorrected and were measured on a Kofler heating plate Type 7841. ^1H NMR spectra were recorded on Bruker WP 200 equipment and the UV-vis spectrum was performed on a Hewlett Packard 8452A diod array spectrometer. Chromatography columns were run on Silica gel Merck No. 7734 and Alumina Merck No. 1097.

(2-Formylphenyl)boronic Acid (4). (a) 2-(*o*-Bromophenyl)-1,3-dioxolane (2). A mixture of 2-bromobenzaldehyde (23.5 mL, 203 mmol), ethylene glycol (13.5 mL, 240 mmol), and *p*-toluenesulfonic acid (1.9 g, 10 mmol) in 150 mL of toluene was refluxed for 6 h. Water formed during reflux was removed with a Dean-Stark apparatus. Evaporation of the solvent and filtration of the crude product over silica gel yielded 40.7 g (179 mmol, 88%) of 2 as a yellow oil.

(b) (2-Formylphenyl)boronic Acid (4). To a slight excess of Mg (2.4 g, 99 mmol) was added dropwise the bromide 2 (20.5 g, 90 mmol) under argon in dry THF. Although the mixture was self-refluxing, the reflux was maintained for an additional 45 min after the end of the addition with an 80 °C oil bath. The cooled solution was transferred to a degassed solution of trimethylborate (20 mL, 176 mmol) in 200 mL of dry THF at –78 °C. The reaction mixture was stirred for 2 h and then allowed to warm to room temperature before hydrolysis with 200 mL of 4 N hydrochloric acid. The solvents were removed, and the milky precipitate was taken in 200 mL of H_2O and 200 mL of ether. The organic phase was then extracted twice with 200 mL of 1 M NaOH. The combined aqueous extracts were acidified to pH 1 with concentrated HCl before extraction with two portions of ether. Evaporation of the solvent yielded 8.4 g (56 mmol, 65%) of the boronic acid 4 as a white foam: mp 108–110 °C; ^1H NMR (200 MHz, δ ppm, ref CD_2HOD) 9.98 (s, 1 H, CHO), 7.93–7.40 (m, 4 H, phenyl), 6.00 (s, 2 H, BOH); mass spectrum (14 eV) M^+ at *m/e* 149 (100). Anal. Calcd for $C_7H_7BO_3$: C, 56.03; H, 4.70. Found: C, 56.02; H, 4.64. If necessary, white crystals could be obtained from cold CH_2Cl_2.

2,9-Bis[*p*-(2-formylphenyl)phenyl]-1,10-phenanthroline (5). To a degassed solution of the dibromide 1 (4.80 g, 9.60 mmol) and 0.07 g (6×10^{-2} mmol) of $Pd(PPh_3)_4$ in 180 mL of toluene were added, under argon, 96 mL of 2 M Na_2CO_3 and a solution of 4 (4.61 g, 23 mmol) in 24 mL of MeOH. After 12 h of reflux, the organic layer was extracted twice with 200 mL of 2 M Na_2CO_3 containing 10 mL of concentrated NH_4OH and dried over $MgSO_4$. Filtration and evaporation of the solvent yielded a light brown solid purified by chromatography over 120 g of SiO_2 in CH_2Cl_2. Elution with 1–2% EtOAc in CH_2Cl_2 afforded 3.60 g (7.8 mmol 68%) of the dialdehyde 5 as a light yellow crystalline product: mp 237–239 °C; ^1H NMR (200 MHz, δ ppm, ref $CHDCl_2$) 10.12 (s, 2 H, CHO), 8.57 (d, J = 8 Hz, 4 H, H_o), 8.46 (d, J = 8 Hz, 2 H, $H_{4,7}$), 8.25 (d, J = 8 Hz, $H_{3,8}$), 8.06 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 2 H, H_{phenyl}), 7.87 (s, 2 H, $H_{5,6}$), 7.73–7.50 (m, 6 H, H_{phenyl}), 7.60 (d, J = 8 Hz, 4 H, H_m); mass spectrum (14 eV) M^+ at *m/e* 460 (59). Anal. Calcd for $C_{38}H_{24}N_2O_4$: C, 84.42; H, 4.47; N, 5.18. Found: C, 84.54; H, 4.58; N, 5.14.

Porphyrin 7. To a degassed solution containing 0.25 g (0.46 mmol) of 5 were added 0.14 g (0.92 mmol) of the dipyrrylmethane 6 in 1750 mL of CH_2Cl_2, under argon, and 1.0 mL of CF_3COOH. After the solution was stirred for 20 h at room temperature, 0.90 g of DDQ (3.96 mmol) was added and the mixture was refluxed for 2 h under argon. To the cooled solution was added 30 mL of triethylamine before repeated extraction with 500 mL of H_2O, under argon. The organic layer was dried over $MgSO_4$ and filtered, and the CH_2Cl_2 was evaporated to leave 0.85 g of crude product. Flash chromatography of the crude compound over Al_2O_3/CH_2Cl_2 (neutral, activity II-III, diameter 1.25 cm, h = 35 cm) afforded

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0.152 g (19.2 10^{-2} mmol, 42%) of the porphyrin **7** as a purple microcrystalline product: mp over 360 °C; UV-vis λ_{max} nm (ϵ mol·L^{-1}·cm^{-1}) 243 (27000, 284 (46000), 412 (14 × 10^4), 506 (10400), 540 (2600), 580 (3500), 635 (629); ^{1}H NMR (200 MHz, δ ppm ref $CHCl_3$) 10.14 (s, 2 H, $H_{methene}$), 9.24 (d, J = 4 Hz, 4 H, H_b), 8.92 (d, J = 4 Hz, 4 H, H_a), 8.77 (d, J = 6.5 Hz, 2 H, H_c), 7.94 (d, J = 8.5 Hz, 2 H, $H_{4,5}$), 7.91 (m, 6 H, $H_{d,e,f}$), 7.52 (d, J = 8.5 Hz, 2 H, $H_{4,7}$), 7.48 (s, 2 H, $H_{5,6}$), 6.71 (d, J = 8.0 Hz, 4 H, H_o), 6.43 (d, J = 8 Hz, 4 H, H_m), -2.90 (s, 2 H, H_{N-H}); mass spectrum FAB, NBA matrix, I = 233 mV, M^+ at m/e 791.4 (100). Anal. Calcd for $C_{56}H_{42}N_6 \cdot C_7H_8 \cdot {}^5/_2H_2O$: C, 81.55; H, 5.01; N, 9.06. Found: C, 81.77; H, 4.71; N, 8.96.

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Registry No. **1**, 129265-60-7; **2**, 34824-58-3; **3**, 137964-68-2; **4**, 40138-16-7; **5**, 129265-61-8; **6**, 21211-65-4; **7**, 137946-82-8; 2-BrC_6H_4CHO, 6630-33-7.

Pyrazolo[3,4-*c*]pyridazines from Hydrazine and Aminothiophenecarboxylates[1]

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As part of another project we required several thiophene analogues of the protected anthranilic acid hydrazide **1**. Reaction of the 3-aminothiophene-2-carboxylic acid esters **2** with hydrazine gave the expected hydrazides **3** which were easily converted to their benzylidene derivatives **4**. Application of this sequence to the isomeric 2-aminothiophene-3-carboxylic esters **5**, however, failed to yield hydrazides **6** and under more severe conditions led to ring rupture as evidenced by the evolution of H_2S.

This, and a similar observation made by Gewald some years ago,[2] can be rationalized by the decreased reactivity of the carbonyl group to nucleophilic attack due to π-electron donation from the two β-situated heteroatoms. Such reactivity is well-known for a variety of related heterocyclic β-enamino esters.[3]

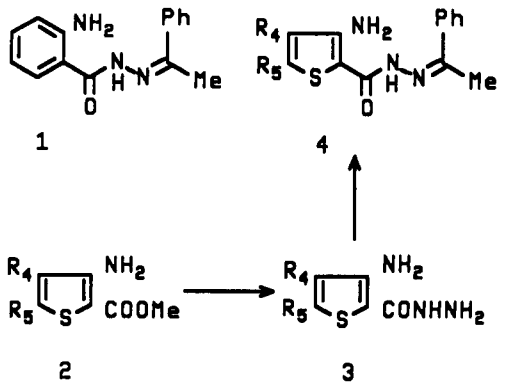
Although the desired protected hydrazides **7** were eventually made by a Gewald cyclization[4] of the protected cyanoacetohydrazide **8**, the nature of the apparent ring-opening reaction was examined further because of the potential utility of such transformations in heterocyclic chemistry.[5]

Results

Esters **5a** and **5b** reacted with 97% hydrazine to give the crude hydrazonium salts **9a** and **9b** in 69 and 87% yield, respectively. Heating the solid salt with soda lime liberated hydrazine while treatment with glacial acetic acid gave the parent amphoteric pyrazolo[3,4-*c*]pyridazines **10a** and **10b** in 64 and 46% overall yield, respectively. The former compound is known but characterized only by its melting point,[6] so structure assignments were based on mass and especially ^{13}C spectra (Table I) which were compared to that of the related pyrazolo[3,4-*c*]pyridazine hydrochloride **10h**·HCl.[7]

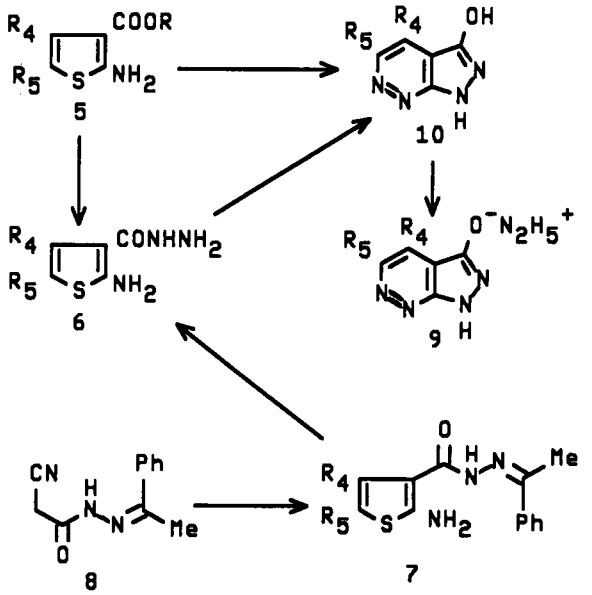
Because formation of this latter compound was the sole example of the transformation **5** → **10** when the five 2-amino-3-carboalkoxythiophenes **5d-h** were treated with

Scheme I[a]



[a] Key: (a) $R_4 = R_5 = H$; (b) $R_4 = R_5 = -CH{=}CHCH{=}CH-$

Scheme II



	R_4	R_5	R
a:	H	H	Me
b:	$-CH_2-CH_2-CH_2-CH_2-$		Et
c:	$-CH_2-CH_2-CH_2-CH_2-$		Me
d:	H	Ph	Et
e:	Ph	H	Et
f:	H	H	?
g:	H	Et	?
h:	H	Me	Me

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