to remove the color. The solution was decanted from the $PbBr_2$ precipitate and added to a cold (ice bath) solution of 23.0 mg (0.11 mmol) of azupyrene in 20 mL of CCl_4. The reaction mixture was stirred for 10 min and then allowed to warm to room temperature.. The solvent was removed (N_2 stream), and the residue was flash chromatographed on a 12 in. × 1 in. silica gel column (5% hexanes in CH_2Cl_2). Three green fractions were collected and analyzed by MS. The first (R_f 0.95) contained azupyrene (m/e 202) plus a trace of bromoazupyrene (m/e 280.282). The second (R_f 0.78) contained thiocyanoazupyrene (m/e 259). The third (R_f 0.62) contained a trace of dithiocyanoazupyrene (m/e 316). The second fraction amounted to 26 mg (91%) of **8** plus **9** in a ratio of 10:1 (high-field ^1H NMR) as a brown solid, mp 165–167 °C: UV–vis (hexanes) λ_{max} (log ϵ) 256 (4.59), 268 (4.71), 291 (4.43), 310 (4.21), 338 (3.99), 351 (3.85), 363 (3.73), 410 (3.33), 456 (3.42), 476 (3.59), 488 nm (4.02); ^1H NMR ($CDCl_3$) [for **8**] δ 7.27 (t, 1, H-9, J = 9.5 Hz), 7.41 (t, 1, H-4), J = 9.5 Hz), 8.30 (s, 2, H-6,7), 8.49 (d, 1, H-10, J = 9.5 Hz), 8.51 (s, 1, H-2), 8.57 (d, 1, H-8, J = 9.5 Hz), 8.62 (d, 2, H-3,5, J = 9.5 Hz), [for **9**] δ 7.47 (t, 1, H-9, J = 9.5 Hz), 8.31 (d, 2, H-1, 7, J = 4.5 Hz), 8.38 (d, 2, H-2,6, J = 4.5 Hz), 8.67 (d, 2, H-8,10, J = 9.5 Hz), 8.80 (s, 2, H-3,5); mass spectrum, m/e (relative intensity) 260 (M^+ + 1, 19), 259 (M^+, 100) 227 (M^+ – 32, 54), 214 (M^+ – 45, 31), 200 (M^+ – 59, 20); exact mass, m/e 259.0456 ($C_{17}H_9SN$ requires 259.0441).

1-(Ethoxymethyl)azupyrene (12).[18] To a solution of 15 mg (0.0374 mmol) of (1-azupyrenylmethyl)trimethylammonium iodide[6] in 4 mL of absolute ethanol was added with stirring 0.4 mL of 0.95 M sodium ethoxide (0.38 mmol) in ethanol. The mixture was refluxed for 1 h and then cooled. The reaction was quenched with 20 mL of H_2O, and the whole was extracted with CH_2Cl_2 (3 × 15 mL). The solvent was removed from the separated, combined, washed (H_2O), and dried (Na_2SO_4) organic layers. Chromatography on a 12 in. × $^1/_2$ in. silica gel column (10% hexanes in CH_2Cl_2) gave a small green band of azupyrene and a second green band which afforded 6.0 mg (62%) of **12** as green needles, mg 61–63 °C after sublimation at 140 °C and 0.3 Torr: UV–vis (hexanes) λ_{max} (log ϵ) 254 (4.67), 267 (4.91), 286 (4.51), 301 (4.26), 311 (4.23), 335 (3.94), 346 (4.07), 358 (3.53), 372 (2.70), 408 (2.85), 442 (3.08), 452 (3.18), 460 (3.08), 472 (3.45), 484 nm (4.03); ^1H NMR ($CDCl_3$), δ 1.33 (t, 3, CH_3, J = 7.1 Hz), 3.71 (q, 2, CH_2, J = 7.1 Hz), 5.39 (s, 2, CH_2), 7.33 (t, 1, H-4, J = 9.5 Hz), 7.38 (t, 1, H-9, J = 9.5 Hz), 8.38 (d, 1, H-6, J = 4.5 Hz), 8.40 (d, 1, H-7, J = 4.5 Hz), 8.41 (s, 1, H-2), 8.62 (d, 1, H-3, J = 9.5 Hz), 8.66 (d, 1, H-5, J = 9.5 Hz), 8.69 (d, 1, H-8, J = 9.5 Hz), 8.73 (d, 1, H-10, J = 9.5 Hz); mass spectrum, m/e (relative intensity) 261 (M^+ + 1, 12), 260 (M^+, 55), 216 (M^+ – 44, 34), 215 (M^+ – 45, 100), 213 (M^+ – 47, 15), 202 (M^+ – 58, 17); exact mass, m/e 260.1200 ($C_{19}H_{16}O$ requires 260.1201).

Dimethyl (1-Azupyrenylmethyl)malonate (13). To the cooled, stirred solution formed by warming 34.4 mg (0.72 mmol) of NaH and 5.0 mL of dimethyl sulfoxide under Ar to 60 °C in a 25-mL flask equipped with a condenser and addition funnel was added 0.17 mL (1.5 mmol) of dimethyl malonate. After 5 min a mixture of 31 mg (0.077 mmol) of (1-azupyrenylmethyl)trimethylammonium iodide[6] and 4.0 mL of dimethyl sulfoxide was added. After heating at 50 °C for 30 min water (5 mL) was added to the cooled mixture and the whole then poured into 50 mL of H_2O and extracted with CH_2Cl_2 (3 × 30 mL). The concentrated (to 50 mL) organic solution was washed (H_2O, 5 × 50 mL) and dried (Na_2SO_4), and the solvent was then removed. Flash chromatography (12 in. × $^1/_2$ silica gel column with 1:1 CH_2Cl_2/benzene) gave, after a small yellow foreband, 22 mg (82%) of **13** as a crystalline yellow solid, mp 93–95 °C after sublimation at 160 °C and 0.2 Torr: UV–vis (CH_3CN) λ_{max} (log ϵ) 253 (4.75), 266 (4.96), 287 (4.57), 302 (4.33), 312 (4.29), 336 (4.03), 346 (4.07), 359 (3.62), 410 (3.00), 442 (3.20), 452 (3.30), 472 (3.49), 484 nm (4.05); ^1H NMR ($CDCl_3$) δ 3.71 (s, 6, CH_3), 4.13 (m, 3, CH, CH_2), 7.34 (t, 1, H-9, J = 9.5 Hz), 7.38 (t, 1, H-4, J = 9.5 Hz), 8.26 (s, 1, H-2), 8.38 (d, 1, H-7, J = 4.5 Hz), 8.40 (d, 1, H-6, J = 9.5 Hz), 8.59 (d, 1, H-10, J = 9.5 Hz), 8.62 (d, 1, H-3, J = 9.5 Hz), 8.65 (d, 1, H-8, J = 9.5 Hz), 8.69 (d, 1, H-5, J = 9.5 Hz); exact mass, m/e 346.1215 ($C_{22}H_{18}O_4$ requires 346.1205).

(18) The procedure was adapted from that used for the preparation of 1-(methoxymethyl)azulene: Anderson, A. G., Jr.; Anderson, R. G., Fujita, T. S. *J. Org. Chem.* **1962**, *27*, 4535.

Nuclear Overhauser Experiments. A $CDCl_3$ solution of a sample containing 69% of **3** and 31% of **2** was subjected to the following sequence at 500 MHz: Irradiate at frequency A (on resonance: 6895.46 Hz for CH_3 of **3**; 6911.31 Hz for CH_3 of **2**) with 40-ms pulse width; delay 0.7 s; observe with 90° pulse at 10 μs; aquire 8K spectrum. Repeat 10 times with two dummy scans. Irradiate at 4217.84 Hz (off resonance) and repeat sequence as described above. Subtract off resonance from on resonance. Repeat for 16 cycles with 1.8-s delay.

A control spectrum of 128 shots and a receiver delay of 2.504 s with two dummy scans was used. The integration parameters were kept constant. % NOE values (3.88 ± 0.08 for H-3 (H-5) of 3, 2.5 ± 0.1% for H-2 of 2) were obtained by dividing the area of the enhanced peak by the area of the peak in the control spectrum and were the average of values determined by plotted integrals and NMR computer digital integration.

Registry No. **1**, 193-85-1; **2**, 109801-96-9; **3**, 109801-97-0; **4**, 109801-98-1; **5**, 109801-99-2; **6**, 102830-03-5; **7**, 102830-04-6; **8**, 109802-00-8; **9**, 109802-01-9; **10**, 72541-89-0; **11**, 95193-27-4; **12**, 109802-02-0; **13**, 109802-03-1; (1-azupyrenylmethyl)trimethylammonium iodide, 102830-08-0.

Synthesis and Crystal Structure of a Novel Tripyrrane-Containing Porphyrinogen-like Macrocycle

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Although a tremendous amount of effort has been devoted to the synthesis and study of tetrapyrrole macrocycles,[1] only a few examples of structurally characterized macrocycles containing a larger or smaller number of pyrroles have been reported.[2-4] Novel pyrrole-containing macrocycles are, nonetheless, currently attracting interest as synthetic targets, either as models for various naturally occurring systems[2,5-7] or because they may display unusual physical,[8-12] chemical,[13,14] or coordination properties.[3,4,15]

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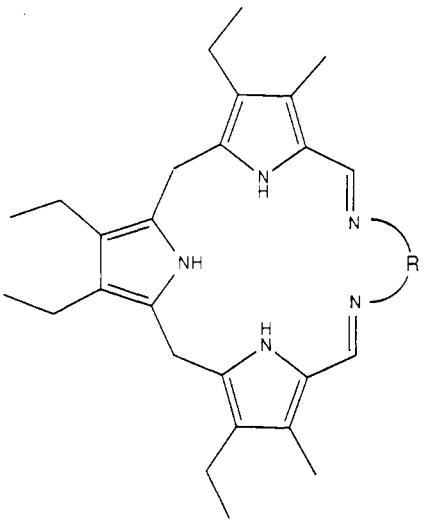
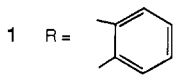
We report here the synthesis of 1 and 2, the first members of a new class of tripyrrane-containing macrocycles, and the single-crystal X-ray structure of 1 in its protonated



1 R =



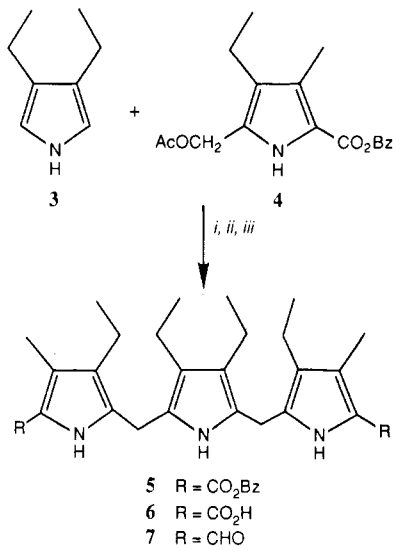
2 R = $-CH_2CH_2CH_2CH_2-$

form. Macrocycles 1 and 2 act as synthetic analogues for the biologically important porphyrinogens,[16,17] systems for which few structurally analyzed models are currently available.[2,6,7]

The key precursor to compound 1, the diformyltripyrrane 7, was synthesized in three steps from simple monomeric pyrroles as shown in Scheme I. Condensation of the pyrroles 3[18] and 4[19] under acidic conditions gave the tripyrrane 5 in 82% yield. Debenzylation by catalytic hydrogenation produced the diacid 6 in quantitative yield. This moderately unstable compound was not characterized, rather it was formylated directly by using the procedure of Clezy[20] to give the dialdehyde 7 in 68% yield. An important aspect of this sequence is the *direct*, acid-catalyzed, synthesis of the tripyrrane skeleton. This approach is considerably more efficient than the stepwise[21] or base-catalyzed[22] procedures reported earlier.

Compounds 1 and 2 were prepared from the acid-catalyzed 1:1 Schiff base condensation of *o*-phenylenediamine or 1,4-diaminobutane, respectively, with the diformyltripyrrane 7 using a synthetic strategy similar to that employed recently by Mertes et al.[15] to effect the 2:2 condensation of diamines with diformyldipyrranes.[23] In

Scheme I[a]



[a] Reagents: (i) EtOH, HCl, 60 °C; (ii) H_2, Pd/C; (iii) trifluoroacetic acid (TFA), 35 °C, followed by triethyl orthoformate at 0 °C.

marked contrast, however, to the dipyrrane case,[15] no macrocyclic products could be isolated in condensations involving the tripyrrane 7 when simple basic metal salts (e.g. $Ba(CO_3)_2$) were used as potential templates. Nor were any products isolated if the reaction was carried out in boiling benzene or MeOH in the absence of a catalyst. Only when an acid catalyst was present and air excluded would the condensations proceed in an acceptable manner. Even then, the yields were extremely sensitive to the reaction conditions employed. With use of the optimized procedure reported in the Experimental Section, compounds 1 and 2 were obtained in 44% and 31% yield, respectively. Yields approaching 70% can, however, be obtained when salts of large cations (i.e. UO_2Cl_2 and $Pb(SCN)_2$) are added in stoichiometric quantities to the Schiff base condensations, *provided that acid catalysis is also employed.* Only the metal-free macrocycles 1 and 2 are isolated when the usual basic workup procedure is employed. If, however, K_2CO_3 is not added during workup, the protonated forms of 1 and 2 are obtained; the crystals of 1·HSCN used for the X-ray diffraction study (see below) were produced in this manner. It is important to note that neither the imine nor pyrrole nitrogens of 1 and 2 are highly basic. Indeed 1·HSCN and 1 display identical TLC and CI mass spectral behavior. Moreover, with the exception of the signals for the pyrrole N-H protons which are shifted to higher field by ca. 1 ppm, the ^1H NMR spectrum of 1·HSCN is essentially identical with that of 1.

In the tripyrrane-containing macrocycles 1 and 2, saturated methylene bridges serve to link the pyrrole subunits. Compounds 1 and 2 are thus structurally related to the porphyrinogens.[16,17] This resemblance is reflected in a number of chemical and spectroscopic properties. For instance, signals for the bridging methylenes appear as a doublet at δ 4.00 and as a broad singlet at δ 3.86 in the ^1H NMR spectra of compounds 1 and 2, respectively. The analogous signals appear at δ 3.80 in the ^1H NMR spectrum of the structurally characterized[7] *N,N′,N″,N‴*-tetramethylporphyrinogen, prepared by Franck and Wegner:[6] The correspondence is even greater in the case of the ^{13}C NMR spectra; all three compounds displays signals for the bridging methylenes at δ 22.3. Compounds 1 and 2 are, of course, not porphyrinogens. They thus

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(23) We have repeated the procedure of Mertes.[15] Even with diamines as large as 1,8-diaminooctane, only 2:2 dimers are obtained; no monomeric macrocyclic adducts analogous to 1 or 2 could be isolated.

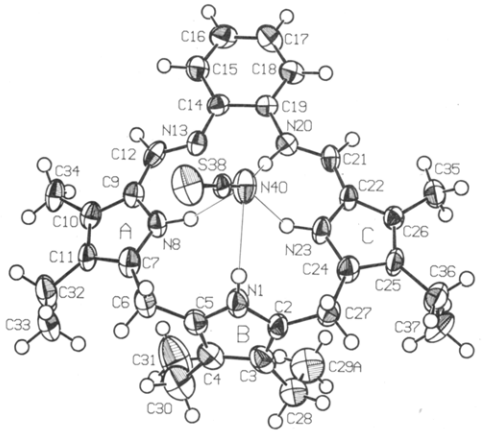

Figure 1. Molecular structure of **1**·HSCN showing the atom labeling scheme. The label for the carbon atom, C39, of the thiocyanate ion has been omitted for clarity. The methyl carbon of the ethyl group bound at C3 is disordered over two principal positions. Only one position, C29A, is shown. N40···H–N hydrogen bond distances (Å): H1, 2.448 (5); H8, 2.199 (6); H20, 2.294 (8); H23, 1.991 (6). N···Ct distances (Å): N1, 3.020 (9); N8, 2.372 (7); N13, 2.448 (8); N20, 2.385 (7); N23, 2.385 (7), where Ct = center of mass of the five macrocyclic nitrogens.

display signals ascribable to the imine protons in the ^{1}H NMR spectra and C=N stretching bands in the infrared region (c.f. Experimental Section).

As is true for the porphyrinogens,[16,17] macrocycles **1** and **2** are nearly colorless compounds showing absorbances only in the UV and not in the visible portion of the electronic spectrum. Moreover, in analogy to the porphyrinogens, compounds **1** and **2** are not thermodynamically stable in air. In marked contrast to the porphyrinogens, however, where air or chemical oxidation leads rapidly to porphyrin formation,[16,17] compounds **1** and **2** react only slowly with air to give as yet uncharacterized decomposition products.[24] Indeed, to date, all attempts to oxidize **1** to the corresponding didehydro conjugated system, using a variety of chemical oxidants, have been unsuccessful.

The observation of a doublet for the bridging methylenes in the ^{1}H NMR of **1** (see above) indicates the presence of diastereotopic protons. This suggests that compound **1** adopts a conformation in solution in which the macrocyclic ring deviates from planarity. The nonplanar structure of **1**·HSCN, determined by X-ray diffraction, is consistent with this analysis (Figure 1). Two main effects contribute to nonplanarity: (1) internal hydrogen bonding to the SCN^- counterion and (2) saturated methylene bridges which preclude conjugation between the central pyrrole (ring B) and the rest of the macrocycle. The nitrogen atom of the thiocyanate ion, N40, is 1.761 (8) Å above the mean plane of the five macrocyclic nitrogen atoms and is directed toward the macrocycle cavity. N40 is within H-bonding distance of the various N-H protons (three pyrroles and the protonated imine N20). All three pyrrole rings are thus tilted toward the capping anion. Hydrogen bonding also forces pyrroles A and C out of the plane of the phenyl ring. This distortion is reflected for the most part in the ca. 13° deviation from ideality observed for the torsion angles about the imine N-phenyl carbon bonds. As a result of the saturated methylene bridges, the central pyrrole ring B is tilted away from the pyrrole rings A and C by angles of 74.6 (3)° and 70.0 (3)°, respectively. These interring dihedral angles are comparable to those observed by Stark et al. for the only other tripyrrane-containing macrocycle reported to date.[2] In this latter system, the analogous dihedral angles are 62.8° and 68.7°. Values in this range were also found for the structurally characterized tetramethylporphyrinogen.[7]

The central 17 atom cavity of **1**·HSCN contains a nearly circular core of five nitrogen atoms. An estimated value of 2.5 Å for the center-to-nitrogen radius may be obtained by projecting the three-dimensional structure onto the mean plane of the five macrocyclic nitrogen atoms. The central cavity of **1**·HSCN thus appears to be larger than that of free-base porphyrins, for which center-to-nitrogen distances of ca. 2.0–2.1 Å are typically observed.[25] In fact, the core radius estimated for **1**·HSCN is nearly identical in value with the average nitrogen-to-center distance (2.53 Å) measured by Day et al. for the uranyl complex of "superphthalocyanine".[3a] The above observations, coupled with the realization that the protonated form of **1** is capable of binding *anions* (e.g. SCN^-), suggest that the tripyrrane-containing macrocycles reported here should be capable of complexing a variety of *metal cations*. Current efforts are therefore being devoted to probing further the binding properties of these potentially pentadentate ligand systems.[26]

Experimental Section

Melting points were recorded on a Mel-temp Laboratory Devices capillary apparatus and are uncorrected. NMR spectra were obtained in $CDCl_3$ with Me_4Si as an internal standard and recorded on either a Varian EM-390 or Nicolet FT-360 spectrometer. Routine and high resolution mass spectra were measured with either a Finnigan MAT 4023 or a Bell and Howell 21-110B instrument. Electronic spectra were recorded in $CHCl_3$ on a Beckman Instruments DU-7. Infrared spectra were recorded, as KBr pellets, from 4000 cm^{-1} to 600 cm^{-1} on a Perkin-Elmer 1320 spectrometer.

2,5-Bis[[5-(benzyloxycarbonyl)-3-ethyl-4-methylpyrrol-2-yl]methyl]-3,4-diethylpyrrole (5). 3,4-Diethylpyrrole (**3**)[18] (0.6 g, 4.9 mmol), benzyl 5-(acetoxymethyl)-3-methyl-4-ethylpyrrole-2-carboxylate (**4**)[19] (2.5 g, 7.9 mmol), and *p*-toluenesulfonic acid (0.15 g) were dissolved in 60 mL of absolute ethanol and heated at 60 °C for 8 h under nitrogen. The resulting suspension was reduced in volume to 30 mL and placed in the freezer for several hours. The product was then collected by filtration, washed with a small amount of cold ethanol, and recrystallized from dichloromethane–ethanol to afford a white powder (2.07 g, 82%): mp 211 °C; ^{1}H NMR δ 0.87 (6 H, t, J = 8 Hz, CH_2CH_3), 1.05 (6 H, t, J = 7 Hz, CH_2CH_3), 2.16 (6 H, s, CH_3), 2.20 (4 H, q, CH_2CH_3), 2.40 (4 H, q, CH_2CH_3), 3.45 (4 H, s, pyrrole$_2$-CH_2), 4.28 (4 H, s, C_6H_5-CH_2), 6.79–7.20 (4 H, br m, aromatic), 7.10 (6 H, m, aromatic), 8.55 (1 H, s, NH), 11.80 (2 H, s, NH); MS, *m/e* (relative intensity) 633 (43), 525 (45), 390 (24), 378 (25), 361 (29), 269 (33), 255 (100); HRMS, 633.3552 (calcd for $C_{40}H_{47}N_3O_4$ 633.3566).

2,5-Bis[(3-ethyl-5-formyl-4-methylpyrrol-2-yl)methyl]-3,4-diethylpyrrole (7). The above diester (4.5 g, 7.1 mmol) was dissolved in 500 mL of dry THF containing 1 drop of triethylamine and hydrogenated over 5% palladium–charcoal (250 mg) at 1 atm H_2 pressure until the reaction deemed complete by TLC. The catalyst was separated and the solution was taken to dryness on the rotorary evaporator. Recrystallization from dichloromethane–hexane yielded **6** (3.2 g, quantitative) as a white powder which quickly develops a red hue upon standing in air: mp 111–115 °C dec. The above diacid (3 g, 6.6 mmol) was dissolved

(24) When left unprotected on the bench top, compound **2** decomposes in a matter of days; compound **1** is far more stable decomposing only over the course of several weeks.

(25) Hoard, J. L. In *Porphyrins and Metalloporphyrins*; Smith, M. K., Ed.; Elsevier: Amsterdam, 1975; Chapter 8.

(26) Preliminary experiments, carried out using $ZnCl_2(H_2O)_2$ as a template in the condensation of *o*-phenylenediamine with **7**, indicate the formation of a 1:1 complex wherein the Zn(II) cation is bound in an η^4 fashion to a ligand resembling **1** in which one of the two bridging methylenes has been oxidized to the methine level. Compound **1** also reacts with $CuCl_2$ to form a 1:1 complex with an as yet unknown constitution. These results will be reported in due course.

in 5 mL of freshly distilled trifluoroacetic acid and heated at reflux for 5 min under nitrogen and allowed to cool to room temperature over the course of 10 min. The above heating and cooling sequence was repeated once more and the resulting dark oil was then cooled in an ice–salt bath. Freshly distilled triethyl orthoformate (5 mL) was then added dropwise with efficient stirring. After 10 min the solution was poured into 300 mL of ice water and let stand 30 min. The dark red precipitate was collected by filtration and washed well with water. Ethanol (ca. 50 mL) was then used to wash the precipitate from the filter funnel into 350 mL of 10% aqueous ammonia. The resulting yellow suspension was stirred well for an hour and then extracted with dichloromethane (5 × 150 mL). The dichloromethane extracts were washed with water, dried over $MgSO_4$, and evaporated to dryness on the rotorary evaporator to give **7** as an off-white mass. Two recrystallizations from chloroform–ethanol gave crystalline product (1.91 g, 68%) with mp 202–203 °C: ^{1}H NMR δ 1.00 (6 H, t, J = 8 Hz, CH_2CH_3), 1.07 (6 H, t, J = 7 Hz, CH_2CH_3), 2.18 (6 H, s, CH_3), 2.35–2.45 (8 H, m, CH_2CH_3), 3.80 (4 H, s, pyrrole$_2$-CH_2), 9.10 (1 H, s, NH), 9.15 (2 H, s, CHO), 9.95 (2 H, s, NH); IR (KBr) 1617 cm^{-1}; MS, m/e (relative intensity) 421 (31), 285 (19), 271 (51), 255 (71), 243 (42), 149 (100); high resolution MS, M^+ 421.27385 (calcd for $C_{26}H_{35}N_3O_2$ 421.27291).

4,5,9,24-Tetraethyl-10,23-dimethyl-13,20,25,26,27-pentaazapentacyclo[20.2.1.1^{3,6}.1^{8,11}.0^{14,19}]heptacosa-3,5,8,10,12,14(19),15,17,20,22,24-undecaene (1). A. Acid-Catalyzed Procedure. The diformyltripyrrane **7** (105 mg, 0.25 mmol) and *o*-phenylenediamine (27 mg, 0.25 mmol) were dissolved, with heating, in a degassed mixture of 300 mL of dry benzene and 50 mL of absolute methanol. Concentrated HCl (0.05 mL) was then added and the resulting gold solution heated at reflux for 24 h under nitrogen. After cooling, solid K_2CO_3 (20 mg) was added and the solution filtered through $MgSO_4$. The solvent was then removed on the rotorary evaporator and the resulting product dissolved in 50 mL of CH_2Cl_2 and refiltered (to remove unreacted **7**). Heptane (100 mL) was added to the filtrate and the volume reduced to 50 mL on the rotorary evaporator whereupon the flask was capped and placed in the freezer overnight. The resulting white powder was then collected by filtration, washed with hexane, and dried in vacuo to yield **1** (55 mg, 44%): mp 188–190 °C dec; ^{1}H NMR δ 1.08 (6 H, t, J = 7 Hz, CH_2CH_3), 1.14 (6 H, t, J = 7 Hz, CH_2CH_3), 2.20 (6 H, s, CH_3), 2.40 (4 H, q, CH_2CH_3), 2.52 (4 H, q, CH_2CH_3), 4.00 (4 H, d, pyrrole$_2$-CH_2), 7.18 (2 H, m, aromatic), 7.47 (2 H, m, aromatic), 8.10 (2 H, s, CHN), 11.12 (1 H, s, NH), 12.08 (2 H, s, NH); ^{13}C NMR δ 9.47, 15.45, 16.57, 17.24, 17.72, 22.32, 116.61, 120.26, 120.74, 125.28, 125.64, 126.80, 134.06, 137.97, 141.99, 142.01; IR 1625 (sh), 1607 cm^{-1}; UV–vis λ_{max} 365 nm; CI MS, $(M + H)^+$ 494; HRMS, M^+ 493.3220 (calcd for $C_{32}H_{39}N_5$ 493.3205).

B. Metal Template Procedure. The diformyltripyrrane tripyrrane **7** and *o*-phenylenediamine reactants were condensed together on a 0.25-mmol scale exactly as described above except that 1.0 equiv of either $Pb(SCN)_2$ (80 mg) or UO_2Cl_2 (85 mg) was added to the boiling solution at the outset of the reaction. Following workup as outlined above, 68 mg (69%) and 60 mg (61%) of **1** were obtained respectively for the Pb^{2+}- and UO_2^{2+}-catalyzed reactions. The products produced in this manner proved identical with that prepared by procedure A.

1·HSCN. The diformyltripyrrane **7** (84 mg, 0.20 mmol), $Pb(SCN)_2$ (64 mg, 0.20 mmol), and *o*-phenylenediamine (22 mg, 0.20 mmol) were dissolved in 300 mL of a boiling mixture of methanol and benzene (1:5 v/v), acidified with 1 drop of concentrated HCl, and heated at reflux for 12 h. The solutions were filtered while hot to remove ca. 50 mg of lead salts and taken to dryness on the rotorary evaporator. The residue was dissolved in 30 mL of CH_2Cl_2 and layered with hexanes. The large red needles which formed over the course of several days were filtered off and air dried (75 mg, 68%). A crystal of approximate dimensions 0.24 mm × 0.24 mm × 0.35 mm was used for the X-ray structure determination (see below). ^{1}H NMR δ 9.79 (1 H, s, NH), 11.52 (2 H, s, NH), all other features as per **1**. The CI MS and TLC chromatographic behavior of this product are identical with those of **1**.

Crystal data: $C_{32}H_{39}N_5$·HSCN, M_r = 552.78, trigonal, space group $R\bar{3}$, (No. 148), on hexagonal axes, a = 33.671 (18) Å, c = 14.934 (10) Å, V = 14663 (15) Å^3, Z = 18, D_m = 1.18 g cm^{-3}, D_x = 1.13 g cm^{-3}, (163 K), $F(000)$ = 5328, Mo Kα radiation, = 0.71069 Å, = 1.227 cm^{-1}. Data were collected on Syntex P2 diffractometer with LT-1 low-temperature attachment and the structure solved by direct methods[27] and refined anisotropically (except disordered methyl atoms C29A and C29B) by full-matrix least-squares procedures.[28] The position of H20 was located from the ΔF map, the other hydrogens were calculated and refined isotropically. R = 0.0794, wR = 0.0585 for 2447 unique reflections with 4° < 2θ < 55° with $F_o > 6(\sigma(F_o))$.

4,5,9,22-Tetraethyl-10,21-dimethyl-13,18,23,24,25-pentaazatetracyclo[18.2.1.1^{3,6}.1^{8,11}]pentacosa-3,5,8,10,12,18,20,22-octaene (2). This compound was prepared by using the same procedures used to prepare **1**. From 100 mg (0.24 mmol) of **7** and 25 L (0.25 mmol) of 1,4-diaminobutane was produced 35 mg (31%) of **2** in the absence of a metal template and 60 mg (53%) when 1 equiv of UO_2Cl_2 was used: mp 152–155 °C dec; ^{1}H NMR δ 1.04–1.11 (12 H, q, CH_2CH_3), 1.75 (4 H, br s, $CH_2CH_2CH_2CH_2$), 2.10 (6 H, s, CH_3), 2.38 (4 H, q, CH_2CH_3), 2.47 (4 H, q, CH_2CH_3), 3.50 (4 H, s, CH_2CHN), 3.86 (4 H, s, pyrrole$_2$-CH_2), 7.84 (2 H, s, CHN); ^{13}C NMR δ 5.77, 9.14, 15.41, 16.46, 17.25, 17.21, 22.34, 26.95, 120.13, 121.88, 122.78, 124.25, 147.80; IR 1640 cm^{-1}; UV–vis λ_{max} 349 nm; HRMS, M^+ 473.3513 (calcd for $C_{30}H_{43}N_5$ 473.3518).

Note Added in Proof: The didehydroconjugated analogue of **1** has now been prepared; by treating **1** with $CdCl_2$ and O_2, the aromatic cadmium complex is obtained.

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Supplementary Material Available: Tables of atomic thermal factors, atomic positional parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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Menthyl 2-Bromocrotonate and Menthyl 4-Bromocrotonate: Reagents for Chiral Vinylogous Darzen and Reformatsky Reactions

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In connection with the development of new methods of asymmetric carbon–carbon bond formation, we required esters **1** and **2** in relatively large amounts and in both optical series. The ethyl analogues of both **1** and **2** have been successfully used in a new vinylcyclopropanation sequence[2] and in the synthesis of functionalized dienes via

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