Cyclovoltammetric Investigation into the Homoconjugation of Plural Pyrazine Rings Linked by Bicyclo[2.2.2]octadiene Spacers

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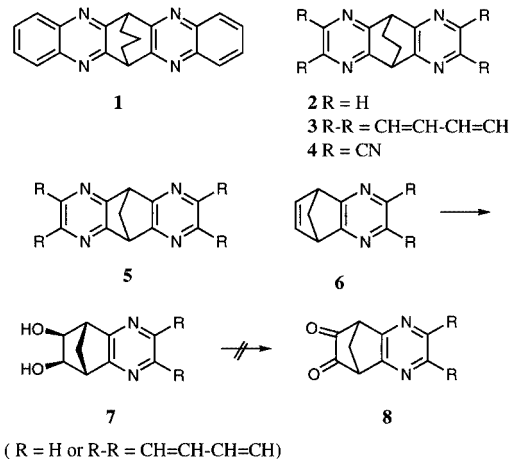
The synthesis and cyclovoltammetric investigation of the ethano-bridged pyrazinoquinoxalines **2**–**4** and the bridged polyazapolyacenes **25**–**27** are described. A large difference between the first and the second reduction potentials for **2**–**4** indicated the presence of strong homoconjugation between the two spatially separated pyrazine rings. The bridged polyazapolyacenes **25**–**27**, on the other hand – with the exception of **27** – exhibited four reduction peaks and the reversibility was found to be poor when compared with that of **2**–**4**.

Introduction

Recent cyclovoltammetric and ESR studies of homoconjugation of two electron-acceptor groups linked by alicyclic rings revealed that delocalization of the unpaired electron in the radical anion state of the bicyclo[3.2.2]nonadiene-fused quinoxaline **1** was rather effective, probably due to its rigid bicyclic structure.[1] We speculated that stronger homoconjugation between two pyrazine rings might be achieved if the length of the bridge in the bicyclic systems were shorter. Except for the quinoxaline **1**, no example of compounds with plural pyrazine or quinoxaline rings incorporated in a bicyclic system has to the best of our knowledge been reported, although the chemistry of pyrazines fused with bicyclic ring systems has received much attention from the viewpoints of the differences in basicities in fused bicyclic skeletons,[2] circular dichroism,[3,4] photochemical reactions,[5−11] electrochemical properties,[12] and the electrophilic reactions of fused norbornadiene systems.[13−15] We thus considered that the pyrazine derivatives **2**−**4** or **5** (Scheme 1) − in which two pyrazine rings are linked by a bicyclo[2.2.2]octadiene or bicyclo[2.2.1]heptadiene skeleton − would be worthwhile to synthesize for investigation of their electrochemical properties. However, our previous attempts to synthesize the diketone **8**, which seems a promising intermediate for the synthesis of **5**, had been unsuccessful because the Swern oxidation of the *exo-cis* diol **7**, prepared from **6**, had resulted in an unexpected ring-opening reaction.[16] The results motivated us to prepare the dipyrazine-fused derivatives **2**−**4**, linked by the bicyclo[2.2.2]-octadiene skeleton, as target molecules with which to investigate homoconjugation between two electron-deficient pyrazine rings, and we wish to describe their synthesis and redox properties here. We also report the synthesis and properties of the bridged polyazapolyacenes **25**−**27**, which had been expected to constitute a novel multi-step redox system.



Scheme 1

Synthesis of Fused Pyrazine Derivatives

A promising synthetic intermediate for the bicyclo[2.2.2]-octadiene-fused pyrazines would be bicyclo[2.2.2]oct-5-ene-2,3-dione (**13**), just as **8** for **5**. Although various methods for the syntheses of substituted bicyclo[2.2.2]oct-5-ene-2,3-diones have been reported,[17−27] the unsubstituted skeleton **13** has uniquely been prepared by means of the Diels−Alder reaction between 1,3-cyclohexadiene (**9**) and dichlorovinylene carbonate, followed by hydrolysis

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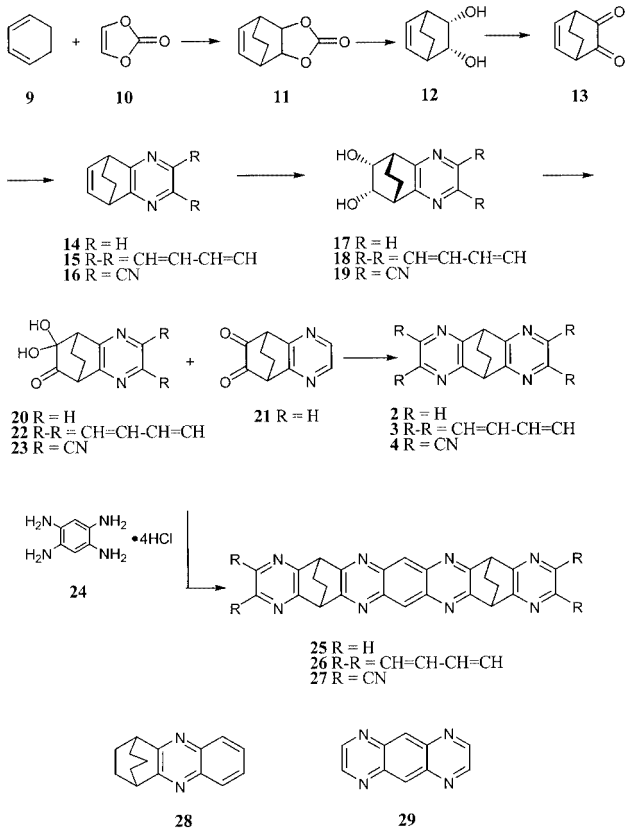

Scheme 2

(Scheme 2).[28] However, the yield of the Diels–Alder reaction has been reported to be rather poor (15%), and a more efficient way to prepare **13** seemed to be required. Recently, Wright and Welker described the synthesis of bicyclo[2.2.2]-octane-2,3-dione by the Swern oxidation of bicyclo[2.2.2]-octane-2,3-diol,[29] available from the Diels–Alder reaction between 1,3-cyclohexadiene (**9**) and vinylene carbonate (**10**), followed by hydrogenation and hydrolysis. The Diels–Alder reaction between **9** with **10** was relatively effective (51% in our hands) compared to that with dichlorovinylene carbonate, and we first investigated the synthesis of **13** by the Swern oxidation of **12**.

The *endo-cis* diol **12** was prepared by hydrolysis of the Diels–Alder adduct **11** by the procedure described in the literature.[30] Swern oxidation[29,31] of **12** with DMSO and trifluoroacetic anhydride successfully gave bicyclo[2.2.2]oct-5-ene-2,3-dione (**13**) in 85% yield. Condensation of **13** with ethylenediamine in the presence of *p*-toluenesulfonic acid, followed by dehydrogenation with nickel peroxide in refluxing benzene, resulted in the formation of 5,8-dihydro-5,8-ethanoquinoxaline **(14)** in 76% yield. The fused quinoxaline **15** was prepared by condensation of **13** with *o*-phenylenediamine as reported previously.[28] Similarly, treatment of **13** with diaminomaleonitrile in dichloromethane at room temperature provided the dicyanopyrazine **16** in 76% yield.

Oxidation of fused pyrazines **14**–**16** with osmium tetroxide in the presence of *N*-methylmorpholine *N*-oxide afforded the *cis* diols **17**–**19** in good yields and as single stereoisomers. X-ray crystallographic analysis of **18** revealed the stereochemistry of the hydroxyl groups to be the *endo-cis* configuration (Figure 1). The exclusive π-facial selectivity in the oxidation would be attributable to the steric effect of the hydrogen atoms on the ethano bridge, which would shield the *exo* face of the double bond, as well as due to the unsymmetrization of π-orbitals.[32–35]

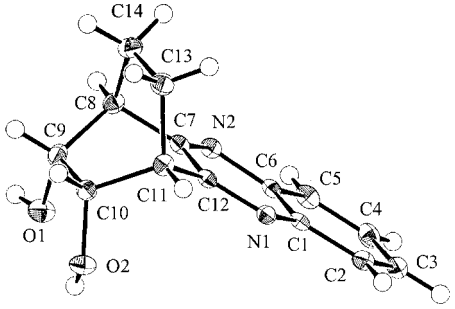

Figure 1. ORTEP drawing of **18**

Swern oxidation of the *cis* diols **17** provided a 5:3 mixture of the hydrate **20** and the diketone **21**. Under the same conditions, the diols **18** and **19** gave the hydrates **22** and **23**, respectively, both containing some inseparable impurities. The formation of a hydrate as a stable product has previously been described for a bicyclo[2.2.2]octanedione derivative.[26] The separation or purification of these mixtures was difficult, and so they were used without purification in the next step. Treatment of the mixture of **20** and **21** with ethylenediamine, followed by oxidation with nickel peroxide, provided **2** in 49% overall yield from **17**. Condensation of **22** with *o*-phenylenediamine afforded **3** (56% from **18**), and treatment of **23** with diaminomaleonitrile similarly provided **4** (60% from **19**).

When 1,2,4,5-tetraaminobenzene tetrahydrochloride (**24**) was used for condensation with **20**–**23** in refluxing acetic acid solutions, the bridged octaazapolyacenes **25**, **26**, and **27**, respectively, were obtained. The use of other solvents such as toluene and dichloromethane in the presence of triethylamine or potassium carbonate resulted in the formation of complex mixtures. These bridged polyazapolyacenes **25**–**27** were obtained as single stereoisomers, judging from the ^{1}H and ^{13}C NMR spectroscopic data. Unfortunately, we were not able to obtain good single crystals for X-ray analysis, and the stereochemistry of these derivatives remained ambiguous.

Cyclic Voltammetric Investigations

The reduction potentials of the fused pyrazine derivatives **2**, **3**, and **4** were measured by cyclic voltammetry in DMF solutions. For comparison, measurements were also conducted for the monopyrazine derivatives **14**, **15**, and **16**. The voltammograms of these derivatives are shown in Figure 2, and their reduction potentials, together with those of the bicyclo[3.2.2]nonadiene-fused derivatives[1] **1** and **28**, are listed in Table 1.

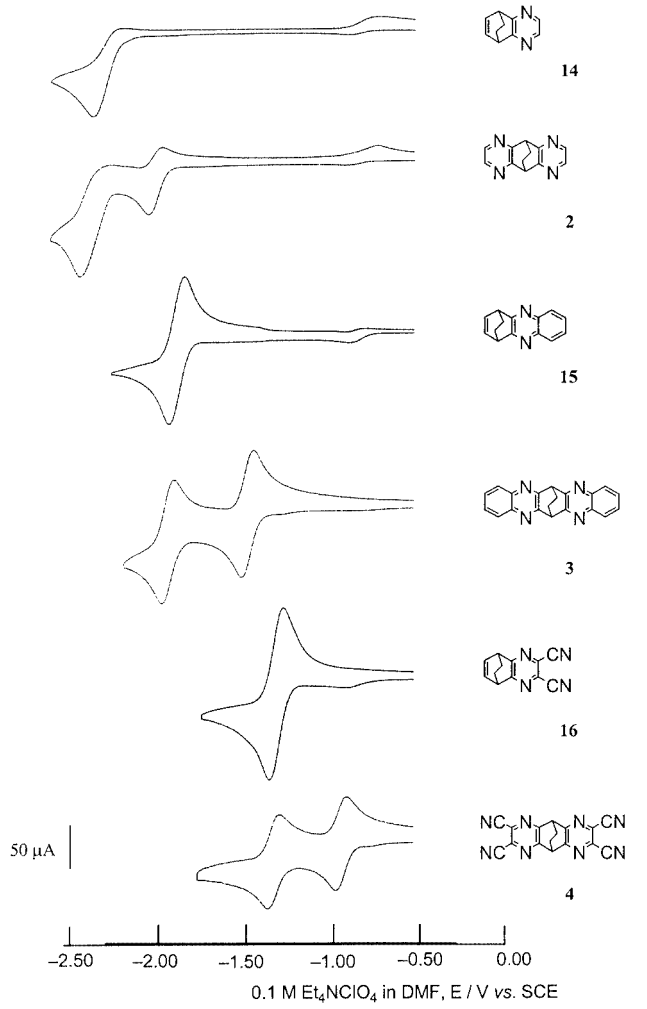

Figure 2. Cyclic voltammograms of the fused pyrazines **2**−**4** and **14**−**16**

Table 1. Reduction potentials (mV) of fused pyrazines **2**−**4** and **14**−**16**, and the differences between the first and second reduction potentials (ΔE) for **14**−**16**

Compound	$E_{red,1}$	$E_{red,2}$	ΔE
14	−2380	–	–
2	−2070	−2470	400
15	−1920	–	–
3	−1530	−1980	450
16	−1320	–	–
4	−970	−1360	390
28[1]	−1820	–	–
1[1]	−1540	−1940	400

The reduction waves observed for these derivatives showed good reversibility, except for those of **14** and the second reduction wave of **2**. The reduction potentials of the dipyrazine-fused derivatives moved to less negative in the order of the fused pyrazine **2**, the quinoxaline **3**, and the dicyanopyrazine **4**. Similar trends were observed for a series of the monopyrazine-fused derivatives **14**, **15**, and **16**. The results indicated that fusion of benzene rings and the substitution of cyano groups on the pyrazine ring generally decreased the reduction potentials of the bridged derivatives. The first reduction peak of **2** appeared in a region less negative by 310 mV while the second reduction peak of **2** shifted to a slightly negative region, relative to that of **14**. The tendencies of the shifts of the first and the second reduction potentials were similar to those between **3** and **15** and between **4** and **16**.

The observation of two reduction peaks for the dipyrazine-fused derivatives **2**, **3**, and **4** suggested that the two spatially separated pyrazine rings were electrochemically inequivalent. The differences between the two reduction potentials for **2**, **3**, and **4** were 400, 450, and 390 mV, respectively. The value for **3** was larger − by 50 mV − even than that for the bicyclo[3.2.2]nonane-fused quinoxaline **1**. The large values of the differences between the first and second reduction peaks indicated delocalization of the unpaired electron in the radical anion state of these derivatives in the two pyrazine rings incorporated in a rigid bicyclo[2.2.2]octane skeleton, possibly by a through-space interaction. Ab initio (HF/6−31G*) calculations on **2** also indicated that the LUMO of **2** displayed mixing of orbitals between two pyrazine rings in the neutral state (Figure 3).[36]

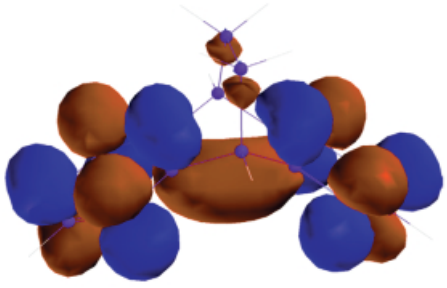

Figure 3. LUMO of the fused pyrazine **2** calculated by ab initio (HF/6−31G*) methods

Cyclic voltammetry measurements for **25** and **26** exhibited the four reduction waves as shown in Figure 4. Unfortunately, the third and forth peaks were irreversible. The cyano-substituted derivatives **27**, on the other hand, only exhibited two irreversible reduction waves, and some decomposition might have taken place during measurements. These results were in contrast to those for the dicyanopyrazine **4**, which displayed completely reversible redox waves. Table 2 summarizes the reduction potentials of the bridged polyazapolyacenes **25**−**27**. The first and second reduction potentials of these derivatives moved to more positive in the order **25**, **26**, and **27**, and the trend seemed to be in agreement with that for the dipyrazine-fused derivatives. The results were also to some extent suggestive of the presence of through-space interactions between heterocyclic nuclei. However, the first and second reduction potentials of **25**−**27** were rather positive in comparison to those of the corresponding dipyrazine-fused derivatives **2**−**4**. These reductions were therefore presumed to be due to the central pyrazinoquinoxaline ring (tetraazaanthracene). Ab initio (HF/6−31G*) calculations on **25** in *syn* or *anti* configura-

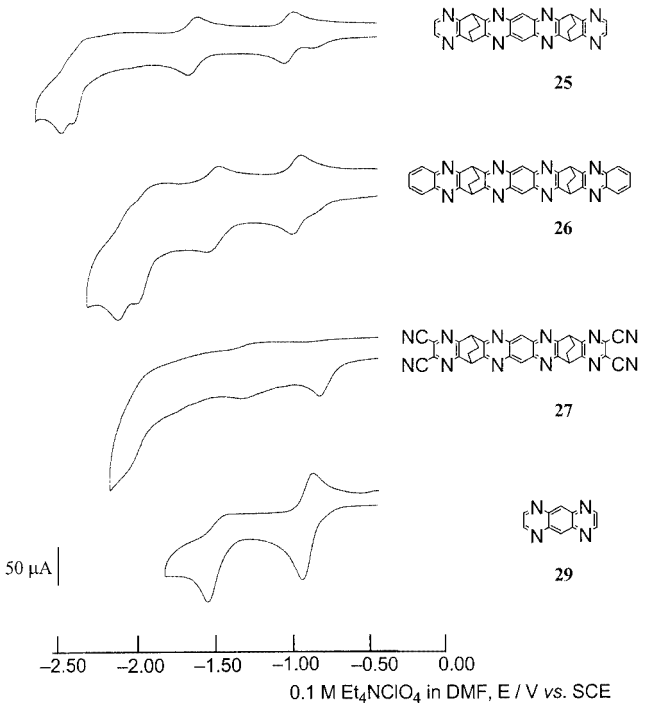

Figure 4. Cyclic voltammograms of the fused pyrazines **25**−**27** and the pyrazinoquinoxaline **29**

Table 2. Reduction potentials (mV) of fused pyrazines **25**−**27** and the pyrazinoquinoxaline **29**

Compound	$E_{red,1}$	$E_{red,2}$	$E_{red,3}$	$E_{red,4}$
25	−1050	−1650	−2400	−2480
26	−1000	−1530	−1990	−2120
27	−810	−1300	−	−
29	−960	−1545	−	−

tions indicated that LUMO coefficients existed only on the central pyrazinoquinoxaline ring.

In order to estimate the reduction potentials of the central pyrazinoquinoxaline nucleus, pyrazino[2,3-*g*]quinoxaline (**29**) was prepared by treatment of tetraaminobenzene **24** with glyoxal. The ESR spectrum of **29** has been reported previously, but no synthetic procedure or physical data were provided.[37] Cyclovoltammetric measurements of **29** under the same conditions showed two reduction waves at −960 mV and −1545 mV; the first wave was reversible and the second one irreversible. The values seemed approximately consistent with the first and second reduction potentials observed for **25**−**27**. These reduction peaks could therefore be attributed to those of the central pyrazinoquinoxaline nucleus, although some perturbation by the fused external pyrazine rings seemed to operate.

Conclusion

Compounds containing plural pyrazine rings with one or two bicyclo[2.2.2]octadiene spacers have been synthesized. Cyclovoltammetric studies on these derivatives suggested that the strong homoconjugation was generally observed for these derivatives, and that the delocalization of an unpaired electron through fusion with a bicyclo[2.2.2]octadiene ring seemed to be more effective than that with a bicyclo[3.2.2]-nonadiene skeleton. On the other hand, the bridged polyazapolyacenes **25** and **26** exhibited four reduction peaks, but their third and forth peaks were irreversible. Furthermore, the fused dicyanopyrazine **27** exhibited only two irreversible reduction waves, in contrast to our expectation of a multiredox system.

Experimental Section

General Remarks: All m.p.′s were determined with a Yanagimoto hot-stage apparatus. IR spectra were obtained with a JEOL Diamond-20 spectrometer. NMR spectra were recorded with a JEOL JNM-LA400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer, with TMS as internal standard. The assignments of the ^{1}H and ^{13}C signals are based on DEPT, H-H COSY, and C-H COSY measurements. Mass spectra were measured with a Shimadzu GCMS-QP1000EX spectrometer operating in electron impact mode (70 eV). Elemental analyses were performed with a Perkin−Elmer Model 240 apparatus. Solvents were dried and purified by standards methods. Yields are based on isolated products of sufficient purity.

X-ray Crystallographic Study: X-ray diffraction data were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with Mo-K_α radiation.

Crystal data for 18: $C_{14}H_{14}N_2O_2$, M = 242.28, monoclinic, space group $P2_1/n$ (no. 14), a = 10.15240(4), b = 9.0012(2), c = 12.6140(6) Å, β = 107.904(2)°, V = 1096.85(7) Å^3, Z = 4, T = 143 K, μ(Mo-K_α) = 1.0 cm^{-1}, 7489 reflections measured, 2011 unique, all of which were used in calculations. The final R_1 was 0.035 [$I > 2.0\ \sigma(I)$] and R_w = 0.109.

CCDC-177887 for **18** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Cyclic Voltammetric Study: Cyclic voltammograms were recorded with a Toho Giken PS-07 electrochemical analyzer, with a glassy carbon disc electrode as the working electrode. A saturated calomel electrode (SCE) and a Pt wire electrode were used as the reference electrode and the counter electrode, respectively. The experiments were carried out under nitrogen with a solution of a sample (1 mM) and Et_4NClO_4 (0.1 mM) as supporting electrolyte. Anhydrous DMF [E_0(Fc/Fc$^+$) = 480 mV] was used as the solvent. The step rate was 100 mVs^{-1}.

Bicyclo[2.2.2]oct-5-ene-2,3-dione (13): Trifluoroacetic anhydride (3.150 g, 15 mmol) was added at −78 °C to a solution of dimethyl sulfoxide (1.362 g, 17.5 mmol) in dichloromethane (30 cm^3). After the mixture had stirred at the same temperature for 10 min, a solution of the diol **12**[30] (0.702 g, 5 mmol) in dichloromethane (10 cm^3) was introduced over 5 min. The mixture was stirred at −78 °C for 2 h. Triethylamine (3.038 g, 30 mmol) was added, and the mixture was stirred for 2 h. The mixture was allowed to warm to

room temperature, and concentrated. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **13** (0.581 g, 85%): yellow powder (from hexane); m.p. 79−80 °C (ref.[28] m.p. 81 °C). IR (KBr): $\tilde{\nu}$ = 3050, 2946, 1745 (C=O), 1236, 1074 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.87 (dm, *J* = 12.0 Hz, 2 H, 7-H and 8-H), 2.06 (dm, *J* = 12 Hz, 2 H, 7-H and 8-H), 3.50 (m, 2 H, 1-H and 4-H), 6.49 (dd,, *J* = 4.5 and 3 Hz, 2 H, 2-H and 3-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.4 (C-7 and C-8), 47.9 (C-1 and C-4), 131.9 (C-2 and C-3), 190.3 (C-5 and C-6) ppm. MS: *m*/*z* (rel. intensity) = 80 (93) [M − 2CO], 79 (100) [C_6H_7], 51 (28) [C_4H_3].

5,8-Dihydro-5,8-ethanoquinoxaline (14): A mixture of the diketone **13** (503 mg, 3.7 mmol), ethylenediamine (333 mg, 5.6 mmol), and *p*-toluenesulfonic acid (68 mg, 0.4 mmol) in benzene (10 cm^3) was stirred at room temperature for 3 h. The mixture was concentrated, and the residue was separated by column chromatography (silica gel, ethyl acetate) to give 5,6,7,8-tetrahydro-5,8-ethanoquinoxaline (586 mg) as a crude oil: IR (neat): $\tilde{\nu}$ = 2942, 2906, 2869, 2844, 1631, 1274, 1101 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.62 (dm, *J* = 11 Hz, 2 H, 9-H_s and 10-H_s), 1.82 (dm, *J* = 11 Hz, 2 H, 9-H_a and 10-H_a), 3.35 (m, 2 H, 5-H and 8-H), 3.45 (m, 4 H, 2-H and 3-H), 6.37 (m, 2 H, 6-H and 7-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.7 (C-9 and C-10), 42.2 (C-2 and C-3), 44.9 (C-5 and C-8), 132.4 (C-6 and C-7), 160.7 (C-4a and C-8a) ppm. MS: *m*/*z* (rel. intensity) = 160 (16) [M^+], 131 (100) [M − C_2H_5], 104 (19) [$C_6H_4N_2$], 77 (20) [C_6H_5].

A mixture of the crude oil (586 mg) and nickel peroxide (3.354 g, 37 mmol) in benzene (30 cm^3) was heated under reflux for 3 h. Insoluble materials were removed by filtration through Celite, and the filtrate was concentrated. The resulting solid was recrystallized form hexane to give **14** (444 mg, 76%) as colorless needles: m.p. 45−46 °C. IR (KBr): $\tilde{\nu}$ = 3046, 2992, 2960, 2942, 2869, 1382, 1095 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.59 (m, 2 H, 9-H_s and 10-H_s), 1.72 (m, 2 H, 9-H_a and 10-H_a), 4.12 (m, 2 H, 5-H and 8-H), 6.56 (dd, *J* = 11 and 3 Hz, 2 H, 6-H and 7-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 24.3 (C-9 and C-10), 42.0 (C-5 and C-8), 134.2 (C-2 and C-3), 139.8 (C-6 and C-7), 158.1 (C-4a and C-8a) ppm. MS: *m*/*z* (rel. intensity) = 158 (17) [M^+], 130 (100) [M − C_2H_4], 103 (38) [$C_6H_3N_2$], 76 (25) [C_6H_4]. $C_{10}H_{10}N_2$: calcd. C 75.92, H 6.37, N 17.71; found C 75.76, H 6.48, N 17.67.

1,4-Dihydro-1,4-ethanophenazine (15): Treatment of the diketone **13** (204 mg, 1.5 mmol) with *o*-phenylenediamine (321 mg, 3 mmol) in dichloromethane (15 cm^3) at room temperature, by the procedure described in the literature,[28] gave **15** (237 mg, 76%) as a white solid: m.p. 145−146 °C (ref.[28] m.p. 147 °C). IR (KBr): $\tilde{\nu}$ = 3052, 2958, 1307, 1099 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.80 (m, 4 H, 11-H and 12-H), 4.20 (m, 2 H, 1-H and 4-H), 6.65 (dd, *J* = 5 and 3 Hz, 2 H, 2-H and 3-H), 7.65 (dd, *J* = 6 and 3 Hz, 2 H, 7-H and 8-H), 7.99 (dd, *J* = 6 and 3 Hz, 2 H, 6-H and 9-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 24.2 (C-11 and C-12), 42.3 (C-1 and C-4), 128.5 (C-7 and C-8), 128.6 (C-6 and C-9), 134.4 (C-2 and C-3), 140.4 (C-5a and C-9a), 158.0 (C-4a and C-10a) ppm. MS: *m*/*z* (rel. intensity) = 208 (56) [M^+], 180 (100) [M − C_2H_4].

5,8-Dihydro-5,8-ethanoquinoxaline-2,3-dicarbonitrile (16): A solution of the diketone **13** (190 mg, 1.4 mmol) and diaminomaleonitrile (196 mg, 1.8 mmol) in dichloromethane (15 cm^3) was stirred at room temperature for 3 h. After removal of the solvent, the residue was separated by column chromatography (silica gel, hexane/ethyl acetate, 1:1) to give **16** (222 mg, 76%): colorless needles (from hexane/ethyl acetate, 5:1); m.p. 250−251 °C. IR (KBr): $\tilde{\nu}$ = 3072, 2948, 2240 (CN), 1365, 1311 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.65 (dm, *J* = 12 Hz, 4 H, 9-H_s and 10-H_s), 1.86 (dm, *J* = 12 Hz,2 H, 9-H_a and 10-H_a), 4.28 (m, 2 H, 5-H and 8-H), 6.63 (m, 2 H, 6-H and 7-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.6 (C-9 and C-10), 41.9 (C-5 and C-8), 113.6 (CN), 129.6 (C-2 and C-3), 133.9 (C-6 and C-7), 161.8 (C-4a and C-8a) ppm. MS: *m*/*z* (rel. intensity) = 208 (56) [M^+], 180 (100) [M − C_2H_4]. $C_{12}H_8N_4$: calcd. C 69.22, H 3.87, N 26.91; found C 69.51, H 4.04, N 26.84.

5,6,7,8-Tetrahydro-5,8-ethanoquinoxaline-6*endo*,7*endo*-diol (17): A solution of the ethanoquinoxaline **14** (510 mg, 3.2 mmol), osmium tetroxide (1 mg), and *N*-methylmorpholine *N*-oxide (1.135 g, 9.7 mmol) in a mixture of acetone (3 cm^3) and water (5 cm^3) was stirred at room temperature for 2 h. Sodium hydrogen sulfite (3 mg) and Florisil (5 g) were added to the solution, and the mixture was stirred for 10 min. Insoluble materials were removed by filtration through Celite, and the filtrate was concentrated. The resulting solid was recrystallized from methanol to give **17** (480 mg, 78%) as colorless rods: m.p. 137−138 °C. IR (KBr): $\tilde{\nu}$ = 3384 (OH), 3058, 2971, 2954, 2917, 1411, 1120 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.50 (dd, *J* = 12 and 5 Hz, 2 H, 9-H_s and 10-H_s), 1.83 (dd, *J* = 12 and 5 Hz, 2 H, 9-H_a and 10-H_a), 3.44 (s, 2 H, 5-H and 6-H), 3.73 (br s, 2 H, 6-OH and 7-OH, disappeared by D_2O addition), 4.29 (s, 2 H, 6-H and 7-H), 8.35 (s, 2 H, 2-H and 3-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.0 (C-9 and C-10), 43.7 (C-5 and C-8), 69.8 (C-6 and C-7), 142.5 (C-2 and C-3), 155.2 (C-4a and C-8a) ppm. MS: *m*/*z* = 192 (36) [M^+], 163 (26) [M − C_2H_5], 133 (100) [M − C_2H_5NO], 77 (27) [C_6H_5]. $C_{10}H_{12}N_2O_2$: calcd. C 62.49, H 6.29, N 14.57; found C 62.51, H 6.38, N 14.73.

1,2,3,4-Tetrahydro-1,4-ethanophenazine-2*endo*,3*endo*-diol (18): Treatment of the ethanophenazine **15** (62 mg, 0.3 mmol) by a procedure similar to that described for **17** gave **18** (72 mg, 99%): white solid (from methanol); decomp. 252 °C. IR (KBr): $\tilde{\nu}$ = 3376 (OH), 3143, 2946, 1243, 1120 cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.45 (d, *J* = 8 Hz, 2 H, 11-H_s and 12-H_s), 1.89 (d, *J* = 8 Hz, 2 H, 11-H_a and 12-H_a), 3.27 (s, 2 H, 1-H and 4-H), 4.18 (s, 2 H, 2-H and 3-H), 4.47 (s, 2 H, 2-OH and 3-OH, disappeared on addition of D_2O), 7.72 (m, 2 H, 7-H and 8-H), 8.00 (m, 2 H, 6-H and 9-H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 20.7 (C-11 and C-12), 43.9 (C-1 and C-4), 68.8 (C-2 and C-3), 128.4 (C-6, C-7, C-8, and C-9), 141.7 (C-5a and C-9a), 156.6 (C-4a and C-10a) ppm. MS: *m*/*z* (rel. intensity) = 242 (63) [M^+], 213 (35) [M − C_2H_5], 183 (100) [M − C_2H_5NO], 102 (19) [$C_6H_3N_2$], 77 (27) [C_6H_5]. $C_{14}H_{14}N_2O_2$: calcd. C 69.41, H 5.82, N 11.56; found C 69.41, H 6.01, N 11.42.

5,6,7,8-Tetrahydro-6*endo*,7*endo*-dihydroxy-5,8-ethanoquinoxaline-2,3-dicarbonitrile (19): Treatment of the ethanoquinoxalinedicarbonitrile **16** (208 mg, 1 mmol) by a procedure similar to that described for **17** gave **19** (207 mg, 86%): white solid (from chloroform); decomp. 195 °C. IR (KBr): $\tilde{\nu}$ = 3559−3318 (OH), 2973, 2238 (CN), 1301, 1116 cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.38 (d, 2 H, *J* = 12 Hz, 9-H_s and 10-H_s), 1.90 (d, *J* = 12 Hz, 2 H, 9-H_a and 10-H_a), 3.35 (s, 2 H, 5-H and 8-H), 4.18 (s, 2 H, 6-H and 7-H), 4.83 (s, 2 H, 6-OH and 7-OH, disappeared on addition of D_2O) ppm. ^{13}C NMR ([D_6]DMSO): δ = 19.8 (C-9 and C-10), 44.3 (C-1 and C-4), 68.8 (C-2 and C-3), 114.4 (CN), 130.9 (C-6 and C-7), 160.6 (C-4a and C-8a) ppm. MS: *m*/*z* (rel. intensity) = 242 (63) [M^+], 213 (35) [M − C_2H_5], 183 (100) [M − C_2H_5NO], 102 (19) [$C_6H_3N_2$], 77 (27) [C_6H_5]. $C_{12}H_{10}N_4O_2$: calcd. C 59.50, H 4.16, N 23.13; found C 59.67, H 4.43, N 23.09.

5,10-Dihydro-5,10-ethanopyrazino[2,3-*g*]quinoxaline (2): A solution of DMSO (183 mg, 2.3 mmol) in dichloromethane (10 cm^3) was cooled at −78 °C, and trifluoroacetic anhydride (428 mg, 2 mmol) was added dropwise over 3 min. To the cooled solution was added

a solution of **17** (130 mg, 0.67 mmol) in a mixture of dichloromethane and DMSO (2:1, 10 cm^3), over 10 min. The mixture was stirred at −78 °C for 6 h, and triethylamine (404 mg, 4 mmol) was introduced. After stirring for 3 h at −78 °C, the mixture was allowed to warm to room temperature and concentrated. The residue was separated by column chromatography (silica gel, ethyl acetate) to give a 5:3 mixture (103 mg) of 1,4-dihydro-3,3-dihydroxy-1,4-ethanoquinoxalin-2-one (**20**) and 1,4-dihydro-1,4-ethanoquinoxaline-2,3-dione (**21**) as yellow needles: m.p. 195−197 °C. IR (KBr): $\tilde{\nu}$ = 3156 (OH), 1752 (CO) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.51 (tt, *J* = 12 and 3 Hz, 0.63 H, **20** 10-H_s), 1.78 (tt, *J* = 12 and 3 Hz, 0.63 H, **20** 9-H_s), 2.01 (dm, *J* = 12 Hz, 0.74 H, **21** 9-H_s and 10-H_s), 2.13 (tm, *J* = 12 Hz, 0.63 H, **20** 9-H_a), 2.29 (tm, *J* = 12 Hz, 0.63 H, **20** 10-H_a), 2.37 (dm, *J* = 12 Hz, 0.74 H, **21** 9-H_a and 10-H_a), 3.41 (t, *J* = 3 Hz, 0.63 H, **20** 4-H), 3.68 (t, *J* = 3 Hz, 0.63 H, **20** 1-H), 4.12 (t, *J* = 2.0 Hz, 0.74 H, **21** 1-H and 4-H), 6.55 (s, 0.63 H, **20** 3-OH, disappeared on addition of D_2O), 6.85 (s, 0.63 H, **20** 3-OH, disappeared on addition of D_2O), 8.42 (d, *J* = 3.0 Hz, 0.63 H, **20** 6-H or 7-H), 8.46 (d, *J* = 3.0 Hz, 0.63 H, **20** 7-H or 6-H), 8.56 (s, 0.74 H, **21** 6-H and 7-H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 19.1 (**20** C-10), 21.1 (**21** C-9 and C-10), 22.3 (**20** C-9), 49.6 (**20** C-4), 53.2 (**20** C-1), 54.3 (**21** C-1 and C-4), 90.2 (**20** C-3), 142.9 (**20** C-6 or C-7), 143.3 (**20** C-6 or C-7), 144.7 (**21** C-6 and C-7), 150.4 (**20** C-4a), 150.5 (**21** C-4a and C-8a), 156.1 (**20** C-8a), 189.5 (**21** C-2 and C-3), 205.2 (**20** C-2) ppm. MS: *m*/*z* = 188 (2) [**21** M^+], 178 (10) [**20** M − C_2H_4], 132 (100) [**21** M − CO − C_2H_4], 104 (16) [$C_6H_4N_2$], 78 (20) [C_6H_6].

A solution of the mixture (103 mg) of **20** and **21**, ethylenediamine (60 mg, 1 mmol), and *p*-toluenesulfonic acid (12 mg, 0.07 mmol) in benzene (5 cm^3) was stirred at room temperature for 2 h. The mixture was concentrated, and the residue was separated by column chromatography (silica gel, ethyl acetate) to give 1,2,3,4,5,10-hexahydro-5,10-ethanopyrazino[2,3-*g*]quinoxaline (73 mg) as a white solid: m.p. 96−98 °C. ^1H NMR ($CDCl_3$): δ = 1.90 (dd, *J* = 12 and 1 Hz, 2 H, 11-H_s and 12-H_s), 2.21 (dd, *J* = 12 and 1 Hz, 2 H, 11-H_a and 12-H_a), 3.45 (dm, *J* = 15 Hz, 2 H, 8-H and 9-H), 3.59 (dm, *J* = 15 Hz, 2 H, 8-H and 9-H), 4.08 (t, *J* = 1 Hz, 2 H, 1-H and 6-H), 8.42 (s, 2 H, 3-H and 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.8 (C-11 and C-12), 44.9 (C-8 and C-9), 48.4 (C-1 and C-6), 143.5 (C-3 and C-4), 153.9 (C-6a and C-10a), 158.5 (C-1a and C-5a) ppm. MS: *m*/*z* (rel. intensity) = 212 (52) [M^+], 183 (100) [M − C_2H_5], 155 (15) [M − $C_2H_4N_2$], 52 (14) [C_4H_4].

A mixture of the white solid (73 mg) and nickel peroxide (607 mg, 6.7 mmol) in benzene (10 cm^3) was heated under reflux for 5 h. Insoluble materials were removed by filtration through Celite, and the filtrate was concentrated. The resulting solid was recrystallized form ethyl acetate to give **2** (70 mg, 49% from **17**) as colorless rods: m.p. 228−230 °C. IR (KBr): $\tilde{\nu}$ = 3073, 2944, 1365, 1095, 1079 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.02 (s, 4 H, 11-H and 12-H), 4.76 (s, 2 H, 1-H and 6-H), 8.30 (s, 4 H, 3-H, 4-H, 8-H, and 9-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 24.2 (C-11 and C-12), 47.6 (C-1 and C-6), 141.7 (C-3, C-4, C-8, and C-9), 155.9 (C-1a, C-5a, C-6a, and C-10a) ppm. MS: *m*/*z* (rel. intensity) = 210 (25) [M^+], 182 (100) [M − C_2H_4], 155 (23) [M − $C_2H_3N_2$], 52 (16) [C_4H_4]. $C_{12}H_{10}N_4$: calcd. C 68.56, H 4.79, N 26.65; found C 68.77, H 4.96, N 26.67.

6,13-Dihydro-6,13-ethanoquinoxalino[2,3-*b*]phenazine (3): A solution of DMSO (109 mg, 1.4 mmol) in dichloromethane (10 cm^3) was cooled at −78 °C, and trifluoroacetic acid (257 mg, 1.2 mmol) was added dropwise over 2 min. To the cooled solution was added a solution of **18** (97 mg, 0.4 mmol) in a mixture of dichloromethane and DMSO (2:1, 5 cm^3), over 3 min. The mixture was stirred at −78 °C for 6 h, and triethylamine (243 mg, 2.4 mmol) was introduced. After stirring for 2 h at −78 °C, the mixture was allowed to warm to room temperature and concentrated. The residue was separated by column chromatography (silica gel hexane/ethyl acetate, 1:5) to give 1,4-dihydro-3,3-dihydroxy-1,4-ethanophenazin-2-one (**22**) (72 mg) as a light tan solid: m.p. 238−240 °C. IR (KBr): $\tilde{\nu}$ = 3199 (OH), 1747 (CO) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.69 (tt, *J* = 12 and 3 Hz, 1 H, 12-H_s), 1.95 (tt, *J* = 12 and 3 Hz, 1 H, 11-H_s), 2.25 (tt, *J* = 12 and 3 Hz, 1 H, 11-H_a), 2.38 (tt, *J* = 12 and 3 Hz, 1 H, 12-H_a), 3.54 (t, *J* = 3.0 Hz, 1 H, 4-H), 3.85 (t, *J* = 3.0 Hz, 1 H, 1-H), 6.70 (s, 1 H, 3-OH, disappeared on addition of D_2O), 7.01 (s, 1 H, 3-OH, disappeared on addition of D_2O), 7.80 (m, 2 H, 7-H and 8-H), 8.06 (m, 2 H, 6-H and 9-H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 18.9 (C-12), 22.6 (C-11), 50.2 (C-2), 53.9 (C-1), 91.1 (C-3), 128.5 (C-7 and C-8), 129.1 (C-6 or C-9), 129.4 (C-6 or C-9), 141.5 (C-5a or C-9a), 141.7 (C-9a or C-5a), 151.9 (C-4a), 156.4 (C-10a), 205.0 (C-2) ppm. MS: *m*/*z* (rel. intensity) = 238 (2) [M − H_2O], 182 (100) [M − H_2O − 2CO].

A solution of **22** (72 mg) and *o*-phenylenediamine (36 mg, 0.33 mmol) in acetic acid (10 cm^3) was stirred at room temperature for 3 h. The mixture was concentrated, and the resulting solid was collected by filtration and washed with methanol to give **3** (69 mg, 56% from **18**): white solid (from hexane/chloroform/methanol, 3:2:5); m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3058, 2967, 1498, 1297, 1099 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.27 (d, *J* = 1 Hz, 4 H, 15-H and 16-H), 4.98 (q, *J* = 1 Hz, 2 H, 1-H and 8-H), 7.73 (m, 4 H, 1-H, 5-H, 11-H, and 12-H), 8.07 (m, 4 H, 3-H, 6-H, 10-H, and 13-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 24.2 (C-15 and C-16), 48.7 (C-1 and C-8), 128.9 (C-4, C-5, C-10, and C-11), 129.6 (C-3, C-6, C-10, and C-13), 141.5 (C-2a, C-6a, C-9a, and C-13a), 155.0 (C-1a, C-7a, C-8a, and C-14a) ppm. MS: *m*/*z* (rel. intensity) = 310 (37) [M^+], 282 (100) [M − C_2H_4]. $C_{20}H_{14}N_4$: calcd. C 77.40, H 4.55, N 18.05; found C 77.40, H 4.64, N 17.76.

5,10-Dihydro-5,10-ethanopyrazino[2,3-*g*]quinoxaline-2,3,7,8-tetracarbonitrile (4): A solution of DMSO (191 mg, 2.4 mmol) in dichloromethane (10 cm^3) was cooled at −78 °C, and trifluoroacetic anhydride (448 mg, 2.1 mmol) was added dropwise over 2 min. To the cooled solution was added a solution of **19** (170 mg, 0.7 mmol) in a mixture of dichloromethane and DMSO (2:1, 5 cm^3), over 3 min. The mixture was stirred at −78 °C for 3 h, and triethylamine (422 mg, 4.2 mmol) was introduced. After stirring for 2 h at −78 °C, the mixture was allowed to warm to room temperature and concentrated. The residue was separated by column chromatography (silica gel, hexane/ethyl acetate, 1:2) to give a mixture (130 mg) containing **23** as a light tan solid: m.p. 165−167 °C. IR (KBr): $\tilde{\nu}$ = 3450 (OH), 2242 (CN), 1764 (CO) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.61 (m, 1 H, 10-H_s), 1.87 (m, 1 H, 9-H_s), 2.27 (m, 2 H, 9-H_a and 10-H_a), 3.57 (t, *J* = 2 Hz, 1 H, 4-H), 3.94 (t, *J* = 2 Hz, 1 H, 1-H), 6.95 (br s, 1 H, 3-OH), 7.22 (br s, 1 H, 3-OH).

A solution of the light tan solid (130 mg) and diaminomaleonitrile (72 mg, 0.67 mmol) in toluene (7 cm^3) was heated under reflux for 26 h. The mixture was concentrated, and the residue was separated by column chromatography (silica gel, hexane/ethyl acetate 1:1) to give **4** (130 mg, 60% from **19**): light yellow solid (from methanol); m.p. 215−217 °C. IR (KBr): $\tilde{\nu}$ = 3014, 2965, 2946, 2242 (CN), 1463, 1353, 1120 cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 2.07 (s, 4 H, 11-H and 12-H), 5.05 (s, 2 H, 5-H and 10-H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 22.3 (C-11 and C-12), 46.7 (C-5 and C-10), 113.9

(CN), 130.9 (C-2, C-3, C-7, and C-8), 157.3 (C-4a, C-5a, C-9a, and C-10a) ppm. MS: *m/z* (rel. intensity) = 310 (37) [M^+], 282 (100) [$M - C_2H_4$]. $C_{16}H_6N_8$: calcd. C 61.94, H 1.95, N 36.11; found C 62.15, H 2.20, N 36.04.

1,4,6,8,10,13,15,17-Octaaza-5,9,14,18-tetrahydro-5,18:9,14-diethanoheptacene (25): A solution of **24** (71 mg, 0.25 mmol) and the mixture of **20** and **21** (77 mg), prepared from **17** (96 mg, 0.5 mmol) by the Swern oxidation reaction as described above, in acetic acid (10 cm^3) was heated under reflux for 30 min. Insoluble materials were removed by filtration, and the filtrate was concentrated. The resulting solid was separated by column chromatography (silica gel, ethyl acetate) to give a light yellow solid, which was recrystallized from chloroform to give **25** (27 mg, 24% from **17**) as a slightly yellow solid: m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 2946, 1382, 1092 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 2.10 (m, 4 H, 19-H, 20-H, 21-H, and 22-H), 2.20 (m, 4 H, 19-H, 20-H, 21-H, and 22-H), 4.76 (s, 4 H, 5-H, 9-H, 14-H, and 18-H), 8.46 (s, 4 H, 2-H, 3-H, 11-H, and 12-H), 8.68 (s, 2 H, 7-H and 16-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 23.3 (C-19, C-20, C-21, and C-22), 47.4 (C-5, C-9, C-14, and C-18), 127.1 (C-2, C-3, C-11, and C-12), 139.2 (C-7 and C-16), 142.7 (C-6a, C-7a, C-15a, and C-16a), 154.5 (C-5a, C-8a, C-14a, and C-17a), 156.9 (C-4a, C-9a, C-13a, and C-18a) ppm. MS: *m/z* = 442 (49) [M^+], 414 (91) [$M - C_2H_4$], 386 (100) [$M - C_3H_6N$]. $C_{26}H_{18}N_8$: calcd. C 70.58, H 4.10, N 25.32; found C 70.83, H 4.36, N 25.33.

1,6,8,10,12,17,19,21-Octaaza-7,11,18,22-tetrahydro-7,22:11,18-diethanononacene (26): A solution of **24** (28 mg, 0.1 mmol) and **22** (48 mg), prepared from **18** (48 mg, 0.2 mmol) by the Swern oxidation reaction as described above, in acetic acid (10 cm^3) was heated under reflux for 30 min. Insoluble materials were removed by filtration, and the filtrate was concentrated. The resulting solid was separated by TLC (silica gel, hexane/ethyl acetate 1:19) to give a tan solid, which was recrystallized from DMSO to give **26** (28 mg, 52% from **18**) as a light tan solid: m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 2950, 1292, 1099 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 2.28 (m, 8 H, 23-H, 24-H, 25-H, and 26-H), 4.88 (s, 4 H, 7-H, 11-H, 18-H, and 22-H), 7.80 (dd, *J* = 6 and 3 Hz, 4 H, 3-H, 4-H, 14-H, and 15-H), 8.07 (dd, *J* = 6 and 3 Hz, 4 H, 2-H, 5-H, 13-H, and 16-H), 8.74 (s, 2 H, 9-H and 20-H) ppm. MS: *m/z* = 542 (41) [M^+], 514 (100) [$M - C_2H_4$], 486 (58) [$M - C_3H_6N$]. $C_{34}H_{22}N_8$: calcd. C 75.26, H 4.09, N 20.65; found C 75.10, H 4.23, N 20.83.

1,4,6,8,10,13,15,17-Octaaza-5,9,14,18-tetrahydro-5,18:9,14-diethanoheptacene-2,3,11,12-tetracarbonitrile (27): A solution of **24** (21 mg, 0.075 mmol) and **23** (34 mg), prepared from **19** (36 mg, 0.15 mmol) by the Swern oxidation reaction as described above, in acetic acid (10 cm^3) was heated under reflux for 30 min. Insoluble materials were removed by filtration, and the filtrate was concentrated. The resulting solid was separated by column chromatography (silica gel, ethyl acetate) to give a light tan solid, which was recrystallized from methanol to give **27** (14 mg, 36% from **19**) as a light yellow solid: m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 2950, 1294, 1099 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 2.15 (m, 4 H, 19-H, 20-H, 21-H, and 22-H), 2.31 (m, 4 H, 19-H, 20-H, 21-H, and 22-H), 4.96 (m, 4 H, 5-H, 9-H, 14-H, and 18-H), 8.79 (s, 2 H, 7-H and 16-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 22.6 (C-19, C-20, C-21, and C-22), 47.5 (C-5, C-9, C-14, and C-18), 114.1 (CN), 131.0 (C-2, C-3, C-11, and C-12), 139.6 (C-7 and C-16), 142.7 (C-6a, C-7a, C-15a, and C-16a), 155.1 (C-5a, C-8a, C-14a, and C-17a), 158.6 (C-4a, C-9a, C-13a, and C-18a) ppm. MS: *m/z* (rel. intensity) = 542 (41) [M^+], 514 (100) [$M - C_2H_4$]. $C_{30}H_{14}N_{12}$: calcd. C 66.42, H 2.60, N 30.98; found C 66.37, H 2.70, N 31.04%.

Pyrazino[2.3-*g*]quinoxaline (29): A solution of 1,2,4,5-tetraaminobenzene tetrahydrochloride (**24**, 212 mg, 0.75 mmol), sodium acetate hydrate (402 mg, 3 mmol), and aqueous glyoxal solution (40%, 218 mg, 1.5 mmol) in ethanol (20 cm^3) was heated under reflux for 30 min. The mixture was concentrated, and water (10 cm^3) and saturated aqueous sodium hydrogen carbonate (20 cm^3) were added to the residue. The mixture was extracted with ether (30 cm^3 × 5), and the combined organic phase was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was separated by column chromatography (silica gel, ethyl acetate) to give **29** (67 mg, 49%): light yellow solid (from hexane/ethanol, 5:1); m.p. 187−189 °C. IR (KBr): $\tilde{\nu}$ = 3062, 3043, 2987, 1579, 1571, 1373, 1218, 997 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.01 (s, 2 H, 5-H, and 10-H), 9.02 (s, 4 H, 2-H, 3-H, 7-H, and 8-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 130.1 (C-5 and C-10), 141.4 (C-4a, C-5a, C-9a, and C-10a), 147.0 (C-2, C-3, C-7, and C-8) ppm. MS: *m/z* (rel. intensity) = 182 (100) [M^+], 155 (28) [$M - CHN$], 128 (60) [$M - C_2H_2N_2$]. $C_{10}H_6N_4$: calcd. C 65.93, H 3.32, N 30.75; found C 65.75, H 3.43, N 30.67.

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