PREPARATION AND STEREOCHEMISTRY OF 1, 4, 8, 11-TETRAAZAPERHYDROPYRENE DERIVATIVES FROM N,N'-BIS(3-AMINOPROPYL)ETHYLENEDIAMINE

Tadashi Okawara*, Hisashi Takaishi, Yoshinari Okamoto, Tetsuo Yamasaki, and Mitsuru Furukawa

Faculty of Pharmaceutical Sciences, Kumamoto University, Oe-hon-machi, Kumamoto 862, Japan

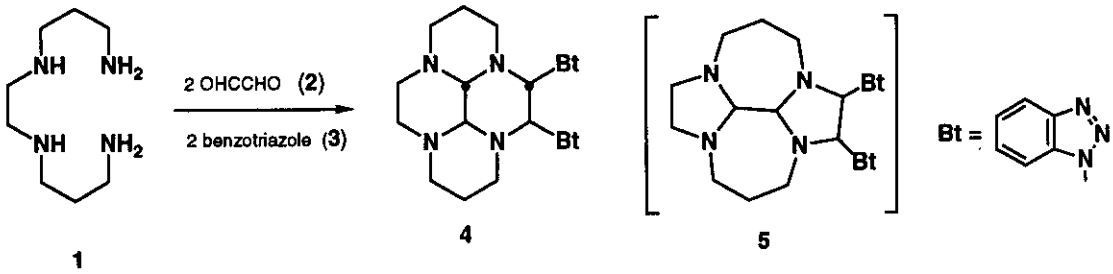
Abstract - The reaction of N,N'-bis(3-aminopropyl)ethylenediamine (**1**) with glyoxal (**2**) in the presence of benzotriazole (**3**) afforded dibenzotriazoyltetraazaperhydropyrene (**4**), which was converted to polyazapolycycles (**6**), (**13**), (**15**), (**16**), and (**19**). The stereochemistry is discussed.

The reaction of linear and cyclic polyamines with glyoxal afforded a variety of bicycles, tricycles, tetracycles, and cage compounds in one-pot reactions.[1-10] Their stereochemistries were fully examined by ^{1}H- and ^{13}C-nmr spectroscopy.

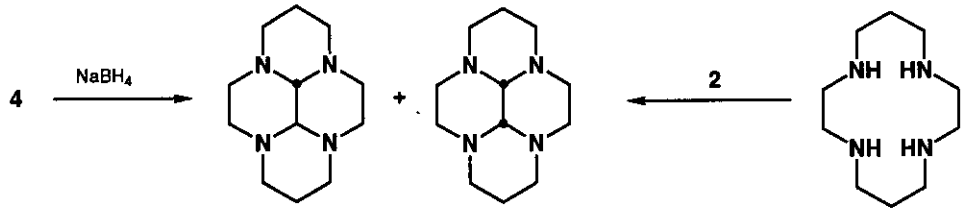
In a continuation of our work on the reaction of polyfunctionalized compounds with dialdehydes,[11-13] we tried to apply Katritzky's method[14-16] using benzotriazole (**3**) to the reaction of N,N'-bis(3-aminopropyl)ethylenediamine (**1**) with glyoxal (**2**) (Scheme 1).

The reaction of **1** with two equivalent of **2** and **3** was carried out in EtOH at room temperature to give dibenzotriazoyltetraazaperhydropyrene (**4**) in 80% yield. The mass spectrum of **4** showed a molecular ion peak at *m/z* 456 which represented the loss of two molecules of H_2O from the sum of **1**, and two equivalents of **2** and **3**. The ^{13}C-nmr spectrum exhibited one half of the total number of carbons (24 carbons) indicating a C_2 symmetry axis. In the ^{1}H-nmr spectrum, two methine hydrogens appeared at δ 3.05 and 5.80 ppm. Another plausible structure (**5**) was eliminated, since this would exhibit 13 carbons in ^{13}C-nmr spectrum.

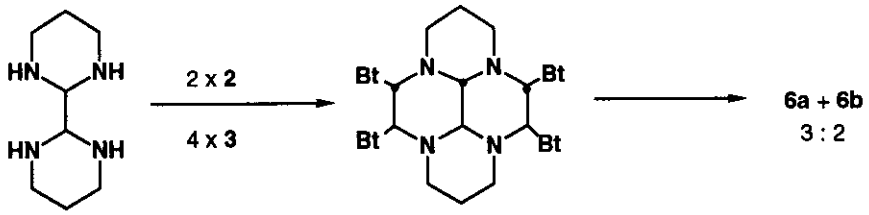
Compound (**4**) was hydrogenolyzed with $NaBH_4$ in THF for removal of two molecules of **3** to give trans and cis tetraazaperhydropyrene (**6a**) and (**6b**) in 50 and 3 % yields, respectively. In the ^{13}C-nmr spectra the



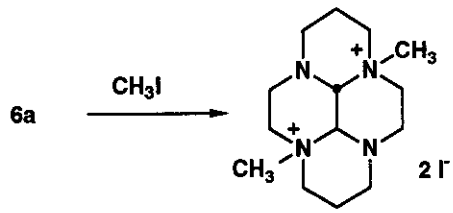
1 4 5



6a 6b 8

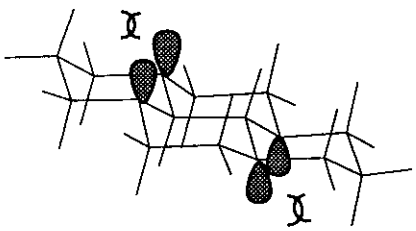


9 10



11

Scheme 1



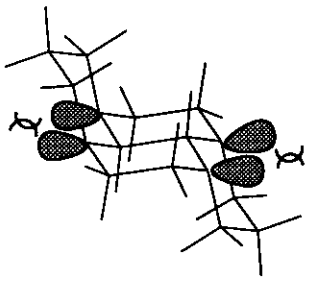
trans fused **6aa**

AM1 ΔHf 44.17 Kcal/mol

trans fused **7aa**

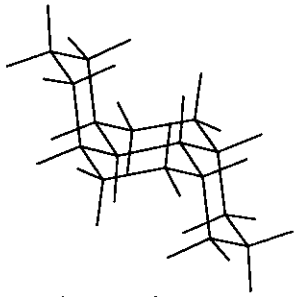
AM1 ΔHf -77.81 Kcal/mol

MM2 ΔHs 19.56 Kcal/mol



cis-trans fused **6ab**

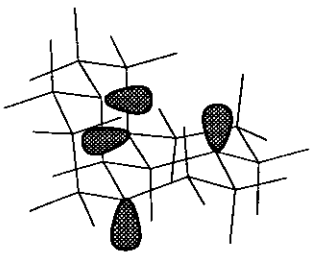
39.17 Kcal/mol



cis-trans fused **7ab**

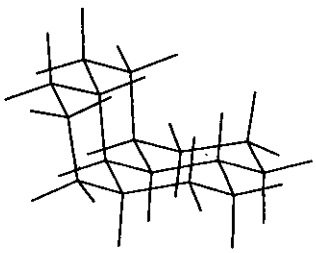
-71.83 Kcal/mol

27.04 Kcal/mol



cis fused **6b**

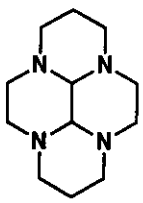
35.82 Kcal/mol



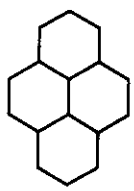
cis fused **7b**

-73.62 Kcal/mol

24.19 Kcal/mol



6



7

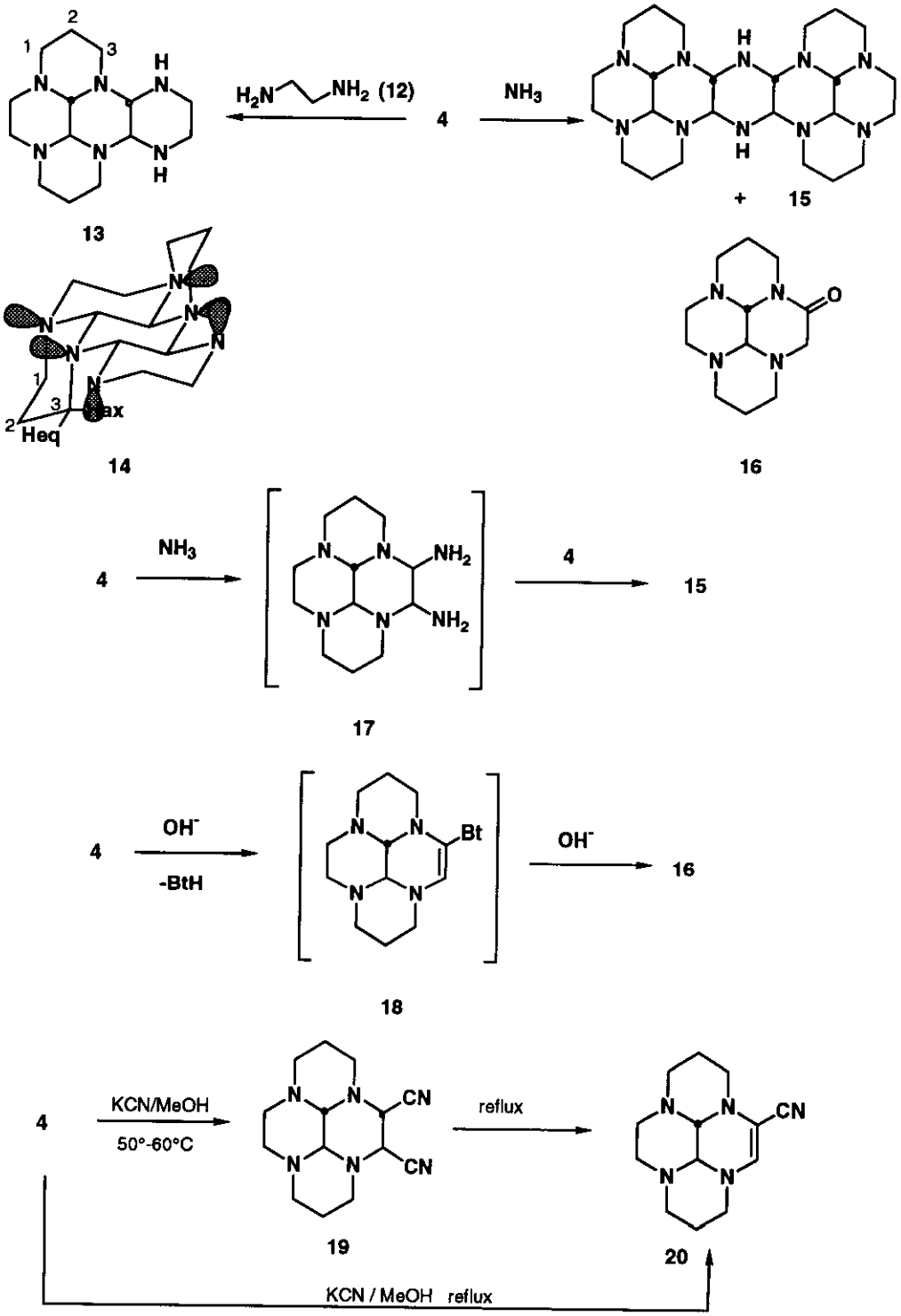
Figure 1 Heats of Formations for Tetraazaperhydropyrene (6) and Perhydropyrene (7)

trans compound (**6a**) showed four carbon signals at δ 24.3, 52.8, 54.2, and 83.7 ppm having two C_2 symmetry axes, while the cis compound (**6b**) indicated six carbons with a single C_2 symmetry axis. The ^{1}H-nmr spectra of **6a** and **6b** indicated methine hydrogens at δ 2.14 and 3.00 ppm, respectively. This shift difference (0.86 ppm) could be attributed to the fact that the hydrogens which are proximal to the lone pair on nitrogen are shifted to lower fields as compared with hydrogens in the opposite direction.[17]

Caulkett[9] reported that the reaction of cyclam (**8**) with **2** afforded **6b** exclusively, the structure of which was determined by X-ray crystallography. Moreover, the trans isomer (**6a**) has two possible stereoisomers, all trans fused form (**6aa**) and cis-trans fused form (**6ab**) as shown in Figure 1. Therefore, in order to study which the most stable form is among three steroisomers (**6aa**, **6ab** and **6b**), the heats of formation (ΔHf) were calculated by MOPAC (AM1). Additionally for the three stereoisomers of pyrene (**7aa**, **7ab**, and **7b**) which have no nitrogen atom, ΔHf and the steric energy (ΔHs) were obtained by AM1 and molecular mechanics (MM2), respectively. The results are summarized in Figure 1. The cis isomer (**6b**) was more stable than either trans isomer (**6aa**) or (**6ab**) by 8.35 and 3.35 Kcal/mol, respectively. Between the two trans isomers, cis-trans fused (**6ab**) was more stable than all trans fused (**6aa**). AM1 calculation for pyrene showed that cis **7aa** was more stable than either trans **7ab** or cis **7b** by 5.98 and 4.19 Kcal/mol, respectively. The ΔHs of pyrene as indicated by MM2 showed that trans fused (**7aa**) is more stable either alternate trans fused (**7ab**) and cis fused **7b** by 7.48 and 4.63 Kcal/mol, respectively. Comparison of ΔHf values for all three stereoisomers suggested that the reaction of cyclam (**8**) with glyoxal proceeded exclusively to avoid repulsive lone-pair lone-pair interactions affording cis **6b**. However, the reaction using **3** proceeded kinetically to give trans isomer (**4**), which was presumed to be preferentially hydrogenolyzed yielding the trans isomer (**6ab**). This simultaneously underwent partial cleavage of the C-N bond to afford the thermodynamically more stable cis isomer (**6b**).

2,2-Bis(hexahydropyrimidine) (**9**)[18] was similarly treated with **2** and **3** to give tetrabenzotriazolyltetraazaperhydropyrene (**10**) which underwent hydrogenolysis yielding compounds (**6a**) and (**6b**) in the ratio of 3:2.

Compound (**6a**) was quarternarized with CH_3I in $CHCl_3$ to produce the dimethylammonium diiodide (**11**) whose structure was determined


H2N NH2 (12)
4
NH3
+ 15
13
14
16
NH3
4
15
17
OH-
-BtH
Bt
18
KCN/MeOH
50°-60°C
reflux
19
20
KCN / MeOH reflux

Scheme 2

spectrally.

Next, the reaction of **4** with ethylenediamine (**12**) was carried out in refluxing EtOH to afford hexaazapentacycle (**13**) in 11% yield (Scheme 2). The ir spectrum showed NH absorption at 3220 cm^{-1} and the mass spectrum indicated a molecular ion peak at *m/z* 279. The ^{13}C-nmr spectrum showed seven carbon signals at δ 24.0, 46.8, 48.2, 53.1, 54.6, 78.6, and 82.6 ppm which indicated a C_2 axis of symmetry. The methylene hydrogens at the 1-position appeared at 1.7 and 3.7 ppm, respectively. This large shift difference (2.0 ppm) is attributed to the direct influence of the nitrogen lone-pair at the 3-position on an axial hydrogen by assuming a stereochemistry having the cis-trans fused form (**14**) similar to the results of **4** and **6**. Compound (**4**) was heated with ammonia in a sealed cylinder to give decaazanonacycle (**15**) and tetraazapyren-5-one (**16**) in 34 and 28% yields, respectively. The Fab-Mass spectrum of **15** indicated a molecular ion at 469 (M^+-2). The ir spectrum showed NH absorptions at 3350 and 3320 cm^{-1}. The ^{13}C-nmr spectrum showed eight methine carbon signals at δ 70.5, 71.6, 74.2, 77.0, 78.8, 82.7, 82.8, and 83.3 ppm indicating the absence of an axis of symmetry. This suggested that the cis-trans fused intermediate (**17**) coupled with **4** to yield **15** which had a slightly twisted central piperazine ring. Compound (**16**) showed carbonyl absorption at 1660 cm^{-1} in ir spectrum and twelve carbons in the ^{13}C-nmr spectrum. It was assumed to form *via* the enamine intermediate (**18**) which was hydrolyzed on work-up to give **16**. Heating of **4** in a methanolic KOH solution easily led to **16** in 65 % yield. Compound (**4**) was treated with KCN in MeOH at 50-60°C to give dicyano compound (**19**) or alternatively refluxed in MeOH to produce monocyano compound (**20**). Compound (**19**) was converted into **20** by refluxing in MeOH. The stereochemistry of **19** was assigned as the cis-trans fused form based on the one half number of carbon atoms in the ^{13}C-nmr spectrum.

The authors acknowledge Dr. K. Harano for AM1 and MM2 calculation.

EXPERIMENTAL

Melting points were determined with a Yanagimoto micro melting point apparatus and are corrected. Ir spectra were recorded with a JASCO IRA-1 grating spectrometer. Nmr spectra were measured with a JEOL spectrometer at 400 MHz for ^1H and at 100 MHz for ^{13}C using a JEOL JNM-GX400 spectrometer. Mass spectra were obtained with a JEOL JMS DX303 mass spectrometer. Calculations of AM1 from MOPAC and MM2 were

performed on the FACOM M-780 computer in Kumamoto University.

5,6-Dibenzotriazoyl-4,7,11,14-tetraazaperhydropyrene (4)-----To a solution of N,N'-bis(3-aminopropyl)ethylenediamine (**1**) (100 mmol, 18.3 ml) and benzotriazole (**3**) (200 mmol, 23.8 g) in EtOH (100 ml) was added slowly glyoxal (**2**) (40% w/v in water, 200 mmol, 29 ml) under cooling with ice and water. After the addition was over, the reaction mixture was stirred for 12 h at room temperature. The separated crystals were collected by filtration and washed with ethanol. mp 178-179°C (from EtOH); Yield 36.5 g(80%); ir (KBr) ν 1615 (C=C) cm^{-1}; ^{1}H-nmr ($CDCl_3$, TMS) δ 1.48-1.51 (2H, m, CHHx2), 1.80-1.90 (2H, m, CHHx2), 2.07-2.13 (2H, m, CHHx2), 2.24-2.28 (2H, m, CHHx2), 2.29-2.32 (2H, m, CHHx2), 2.70 (2H, d, CHHx2, J=8.1 Hz), 2.91 (2H, d, CHHx2, J=8.1 Hz),3.00-3.03 (2H, m, CHHx2), 3.05 (2H, s, CHx2), 5.80 (2H, s, CHx2), 7.34-8.00 (8H, m, Phx2); ^{13}C-nmr ($CDCl_3$, TMS) δ 23.6 (CCC), 49.5 (CCN),52.9 (CCN), 54.0 (NCC), 77.8 (NCBt), 81.8 (NCN), 111.3, 120.4, 124.5, 128.0, 131.3, 146.5 (Ph); ms (EI) m/z 456 (M^+, 10), 337 (47), 309 (100), 219 (80), 199 (75), 119 (60); *Anal.* Calcd for $C_{24}H_{28}N_{10}$: C,63.13; H,6.18; N,30.67. Found: C, 63.27; H,6.40; N, 30.34.

4,7,11,14-Tetraazaperhydropyrene (6)-----To a suspended solution of **4** (5 mmol, 2.28 g) in THF (60 ml) was added sodium borohydride (15 ml, 0.60 g) under cooling with ice and water. The reaction mixture was refluxed for 12 h. Water (20 ml) was added and the solvent was evaporated under reduced pressure. To the resulting residue was added 1 N NaOH (15 ml) and extracted with CH_2Cl_2 (15 mlx5). The combined extract was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by a silica gel column chromatography ($CHCl_3$:MeOH=8:1).

6a: mp 130-131°C; Yield 0.56 g (50%); ^{1}H-nmr ($CDCl_3$, TMS) δ 1.51-1.56 (2H, m, CHHx2), 1.90-2.01 (2H, m, CHHx2), 2.03-2.10 (4H, m, CHHx4), 2.14 (2H, s, CHx2), 2.39-2.47 (4H, m, CHHx4), 2.63-2.72 (4H, m, CHHx4), 2.85-2.89 (4H, m, CHHx4); ^{13}C-nmr ($CDCl_3$, TMS) δ 24.3 (CCC), 52.8 (CCN), 54.2 (NCC), 83.7 (NCN); ms (CI): m/z 223 (M^++1, 100); *Anal.* Calcd for $C_{12}H_{22}N_4$: C,64.83; H,9.97; N,25.20. Found: C,64.87; H,9.95; N, 24.86.

6b: oil; Yield 0.03 g (3%); ^{1}H-nmr ($CDCl_3$, TMS) δ 0.91-1.50 (2H, m), 1.73-3.87 (18H, m), 3.00 (2H, s); ^{13}C-nmr ($CDCl_3$, TMS) δ 19.6 (CCC), 44.8 (CCN), 52.6 (NCC), 54.4 (NCC), 56.1 (CCN), 77.1 (NCN). (lit.[19] δ 19.7 (CCC), 44.9 (CCN), 52.6 (NCC), 54.5 (NCC), 56.1 (CCN), 77.1 (NCN)); HRms (EI) *m/z* Found 222.183. Calcd for $C_{12}H_{22}N_4$ 222.184.

5,6,12,13-Tetrabenzotriazolyl-4,7,11,14-tetraazaperhydropyrene (10)----To a stirred solution of 2,2'-bis(hexahydropyrimidine) (**8**) (21.2 mmol,

3.6 g) in EtOH (60 ml) was added benzotriazole (**3**) (84.7 mmol, 10.2 g) followed by gradual addition of glyoxal (**2**) (40% w/v in water, 42.4 mmol, 6.14 ml) under cooling with ice and water. The reaction mixture was stirred for 12 h at room temperature. The separated solid was collected by filtration, washed with EtOH, and recrystallized from EtOH. mp 196°C (decomp.); Yield 7.72 g (53%); ir (KBr) ν 1620(C=C) cm^{-1}; ms (CI) m/z 689 (M^+-2, 18), 361 (27), 334 (100), 315 (28). *Anal.* Calcd for $C_{36}H_{34}N_{16}$: C;62.60; H,4.96; N;32.44. Found: C,62.93; H,5.08; N, 32.10.

4,11-Dimethyl-4,7,11,14-tetraazaperhydropyrenium diiodide (11)-----A solution of **6a** (3 mmol, 0.66 g) and CH_3I (30 mmol, 3.6 ml) in $CHCl_3$ (30 ml) was stirred for 12 h at 60°C in a sealed cylinder. The separated solid was collected by filtration and recrystallized from EtOH-water. mp 225°C (decomp.); Yield 1.02 g (67%); ^{1}H-nmr ($CDCl_3$, TMS) δ 2.37-2.40 (2H, m, CHHx2), 2.76-2.89 (2H, m, CHHx2), 3.18-3.25 (2H, dt, CHHx2, J=4.0 Hz, 8.4 Hz), 3.54-3.67 (4H, m, CHHx2 and CHHx2), 3.73 (6H, s, CH_3x2), 3.77-3.80 (2H, m, CHHx2), 3.94-4.02 (2H, dt, CHHx2, J=3.7 Hz, 13.2 Hz), 4.11-4.21 (6H, m, CHHx2 and CH_2 x2), 4.63 (2H, s, CHx2); ^{13}C-nmr ($CDCl_3$, TMS) δ 20.9 (CCC), 41.3 (NCH_3), 47.8 (CCN), 54.1 (NCC), 61.6(NCC), 67.8 (CCN), 81.9 (NCN); ms (FAB) m/z 251 (M^++1, 17), 169 (27), 85 (100); *Anal.* Calcd for $C_{14}H_{28}N_4I_2$: C,33.22; H,5.58; N,11.07. Found: C,32.40; H,5.55; N,10.86.

Piperidino[2,3-e]-4,7,11,14-tetraazaperhydropyrene (13)-----To a suspended solution of **4** (5 mmol, 2.28 g) in $CHCl_3$ (60 ml) was gradually added ethylenediamine (**12**) (5 mmol, 0.33 ml) with stirring at room temperature, then the reaction mixture was refluxed for 12 h. After removal of the $CHCl_3$, the resulting residue was solidified by treatment with a small amount of EtOH-*i*-Pr_2O. The solid was dissolved in CH_2Cl_2 (20 ml) and removed unreacted benzotriazole (**3**) with 1 N NaOH (10 ml). The NaOH solution was saturated with NaCl and was extracted with CH_2Cl_2 (15 mlx5). The combined CH_2Cl_2 solution was dried over $MgSO_4$. Removal of CH_2Cl_2 gave a solid which was recrystallized from CH_2Cl_2-*i*-Pr_2O. mp 245°C; Yield 0.15 g (11%); ir (KBr) ν 3220 (NH) cm^{-1}; ^{1}H-nmr ($CDCl_3$, TMS) δ 1.57-1.62 (2H, m, CHHx2), 1.67-1.79 (2H, m, CHHx2), 1.80-1.92 (2H, m, CHHx2), 2.04-2.14 (2H, m, CHHx2), 2.18 (2H, s, NHx2), 2.41 (2H, s, CHx2), 2.44 (2H, d, CHHx2, J=7.6 Hz), 2.62 (2H, s, CHx2), 2.63 (2H, d, CHHx2, J=9.9 Hz), 2.70 (2H, d, CHHx2, J=7.6 Hz), 2.87-2.91 (2H, m, CHHx2), 3.01 (2H, d, CHHx2, J=9.9 Hz), 3.73-3.77 (2H, m, CHHx2); ^{13}C-nmr ($CDCl_3$, TMS) δ 24.0 (CCC), 46.8 (NCC), 48.2 (CCN), 53.1 (CCN),

54.6 (NCC), 78.6 (NCN), 82.6 (NCN); ms (CI) m/z 279 (M^++1, 100), 195 (20); *Anal.* Calcd for $C_{14}H_{26}N_6$: C,60.40; H,9.41; N,30.19. Found: C, 60.17; H,9.41; N,29.91.

Tetrabenzo[*de,jk,op,uv*]-1,4,5,6,7,8,11,12,13,14-decaazaperhydropentacene (15) and 4,7,11,14-tetraazaperhydropyren-5-one (16)-----A solution of **4** (2 mmol, 0.91 g) in saturated methanolic ammonia (40 ml) was stirred for 12 h at 70°C in a sealed cylinder. After removal of the solvent, the residue was dissolved in CH_2Cl_2 (15 ml) and benzotriazole (**3**) was removed by washing with 1 N NaOH (15 ml). The NaOH solution was back-extracted with CH_2Cl_2 (15 mlx4). The combined extract was dried over $MgSO_4$. After removal of the CH_2Cl_2, the residue was purified by a silica-gel column chromatography ($CHCl_3$:MeOH=10:1). The fractions containing **15** was evaporated and the residue was recrystallized from CH_2Cl_2-*i*-Pr_2O.

15: mp 190°C (decomp.); Yield 0.15 g (34%); ir (KBr) ν 3320, 3250 (NH) cm^{-1}; ^{1}H-nmr ($CDCl_3$, TMS) δ 1.55-1.61 (4H, m, C<u>H</u>Hx4), 1.66-1.75 (4H, m, CH<u>H</u>x2 and NHx2), 1.88 (4H, t, C<u>H</u>Hx4, J=12.2 Hz), 1.99-2.07 (4H, m, CH<u>H</u>x4), 2.28-2.35 (3H, m, CHx3), 2.38-2.49 (4H, m, C<u>H</u>Hx4), 2.60 (2H, d, CHx2, J=6.9 Hz), 2.69-2.71 (6H, m, C<u>H</u>Hx2 and CH<u>H</u>x4), 2.86-3.08 (6H, m, C<u>H</u>Hx5 and CH), 3.18 (1H, d, CH, J=2.3 Hz), 3.59-3.62 (2H, m, C<u>H</u>H and CH), 3.72 (1H, d, CHH, J=10.9 Hz), 3.85 (1H, d, C<u>H</u>H, J=12.2 Hz); ^{13}C-nmr ($CDCl_3$, TMS) δ 23.9, 24.0, 24.4 (CCC), 47.8, 48.1, 48.5, 48.6, 52.9, 53.6, 53.2, 53.9, 54.3, 54.6 (CCN), 70.5, 71.6, 74.2, 77.0, 78.8, 82.7, 82.8, 83.3 (NCN); ms (FAB) m/z 469 (M^++1, 65), 275 (25), 234 (78), 220 (100), 195 (55), 152 (42); *Anal.* Calcd for $C_{24}H_{42}N_{10}$ H_2O: C,58.99; H,9.08; N,28.66. Found: C,59.35; H,8.96; N,28.69.

16: oil; Yield 0.13g (28%); ir (KBr) ν 1660 (C=O) cm^{-1}; ^{1}H-nmr ($CDCl_3$, TMS) δ 1.64-1.69 (2H, m, C<u>H</u>Hx2), 1.75-1.79 (1H, m, CH<u>H</u>), 1.93-1.96 (2H, m, C<u>H</u>H and CH<u>H</u>), 2.08-2.24 (2H, m, C<u>H</u>Hx2), 2.41-2.52 (3H, m, CH<u>H</u>x3), 2.45 (1H, d, CH, J=6.6 Hz), 2.77-2.95 (5H, m, C<u>H</u>Hx5), 2.89 (1H, d, C<u>H</u>H, J=16.5H z), 3.36 (1H, d, CH, J=6.6 Hz), 3.47 (1H, d, C<u>H</u>H, J=16.5 Hz), 4.61-4.66 (1H, m, C<u>H</u>H); ^{13}C-nmr ($CDCl_3$, TMS) δ 23.3, 23.9 (CCC), 3.96, 52.8, 53.0, 53.1, 53.4 (CCN), 57.5 (NCC=O), 77.8, 81.6 (NCN), 165.6 (C=O); HRms (CI) (M+1): *m/z* Found 237.1715. Calcd for $C_{12}H_{21}N_4O$ 237.1694; *Anal.* Calcd for $C_{12}H_{20}N_4O$: C,60.99; H,8.53; N,23.71. Found: C,60.75; H,8.34; N; 23.99.

Compound (16) by treatment of 4 with methanolic NaOH solution-----A suspended solution of **4** (2 mmol, 0.91 g) in saturated methanolic NaOH solution (50 ml) was refluxed for 10 h. After removal of MeOH, water

(20 ml) was added to the residue and the resulting product was extracted with CH_2Cl_2 (20 ml x 3). The combined extract was dried over $MgSO_4$, evaporated under reduced pressure, and the residue was purified by the same work up mentioned above to give **16** in 65 % yield. The product was identified with the spectral data of **16**.

5,6-Dicyano-4,7,11,14-tetraazaperhydropyrene (19)-----A suspended solution of **4** (5 mmol, 2.28 g) and KCN (10 mmol, 0.65 g) in EtOH (60 ml) was refluxed for 12 h. After addition of 1 N NaOH (15 ml) to the reaction mixture, EtOH was evaporated, and the remaining solution was extracted with CH_2Cl_2 (15 mlx5). The combined CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by a silica gel column chromatography ($CHCl_3$:MeOH=15:1). mp 116-119°C; Yield 0.76 g (56%); ir (KBr) ν 2220, 2180 (CN) cm^{-1}; ^{1}H-nmr ($CDCl_3$, TMS) δ 1.54-1.59 (2H, m, C<u>H</u>Hx2), 1.85-1.98 (2H, m, CH<u>H</u>x2), 2.01-2.09 (2H, m, C<u>H</u>Hx2), 2.40 (2H, d, CH<u>H</u>x2, J=7.9 Hz), 2.43-2.49 (2H, m, C<u>H</u>Hx2), 2.54 (2H, s, CHx2), 2.64 (2H, d, C<u>H</u>Hx2, J=7.9 Hz), 2.76-2.81 (4H, m, CH<u>H</u>x4), 3.92 (2H, s,CHx2); ^{13}C-nmr ($CDCl_3$, TMS) δ 23.6 (CCC), 51.4 (CCN), 52.7 (CCN), 53.0 (NCC), 54.9 (NCCN), 79.0 (NCN), 113.6 (CN); ms (EI) m/z 272 (M^+,68), 195 (42), 112 (38), 97 (100); *Anal.* Calcd for $C_{14}H_{20}N_6$ H_2O: C,57.91; H,7.64; N,28.94. Found: C,57.95; H, 7.43; N,28.97.

5-Cyano-4,7,11,14-tetraaza-1,2,3,4,4a,7,7a,8,9,10,11,12,13,14-tetradecahydropyrene (20)-----The reaction was carried out under reflux for 12 h by the method described above. The residue was recrystallized from CH_2Cl_2-*i*-Pr_2O. mp 143-144°C; Yield 0.77 g (63%); ir (KBr) ν 2200 (CN), 1640 (C=C) cm^{-1}; ^{1}H-nmr ($CDCl_3$, TMS) δ 1.59-1.70 (2H, m, C<u>H</u>Hx2), 1.85-1.96 (2H, m, CH<u>H</u>x2), 2.11-2.22 (2H, m, C<u>H</u>Hx2), 2.43-2.57 (3H, m, CH<u>H</u>x3), 2.72 (1H, d, CH, J=5.9 Hz), 2.74-2.97 (5H, m, C<u>H</u>Hx1 and CH<u>H</u>x4), 3.01 (1H, d, CH, J=5.9 Hz), 3.22-3.26 (1H, m, C<u>H</u>H), 3.53-3.58 (1H, m, C<u>H</u>H), 6.00 (1H, s, CH); ^{13}C-nmr ($CDCl_3$, TMS) δ 24.0, 24.1 (CCC), 49.2, 50.0 (CCN), 51.9, 52.3 (CCN), 53.2, 53.7 (NCC), 75.6, 77.7 (NCN), 98.1 (NCCN), 117.4 (CN), 130.1 (NC=); ms (CI) m/z 245 (M^++1, 100), 217 (11); *Anal.* Calcd for $C_{13}H_{19}N_5$: C,63.65; H,7.81; N,28.55. Found: C, 63.77; H, 7.89; N,28.43.

REFERENCES

1. M. R. Crampton, J. Hamid, R. Millar, and G. Ferguson, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 923.
2. D. C. Craig, M. Kassiou, and R. W. Read, *J. Chem. Soc., Chem.*

Commun., **1991**, 607.
3. D. S. Black, M. Kassiou, and R. W. Read, *J. Org. Chem.*, 1991, **56,** 4308.
4. A. T. Nielsen, R. A. Nissan, D. J. Vanderah, C. L. Coon, R. D. Gilardi, C. F. George, and J. F. Anderson, *J. Org. Chem.*, 1990, **55,** 1459.
5. R. L. Willer, D. W. Moore, and D. J. Vanderah, *J. Org. Chem.*, 1985, **50,** 2365.
6. R. L. Willer, D. W. Moore, C. K. Lowe-Ma, and D. J. Vanderah, *J. Org. Chem.*, 1985, **50,** 2368.
7. B. Fuchs, S. Weinman, U. Schmueli, A. R. Katritzky, and R. C. Patel, *Tetrahedron Lett.*, 1981, **22**, 354.
8. G. R. Weisman, S. C. H. Ho, and V. Johnson, *Tetrahedron Lett.*, 1980, **21**, 335.
9. P. W. R. Caulkett, D. Greatbanks, R. W. Turner, and J. A. J.Jarvis, *J. Chem. Soc., Chem. Commun.*, **1977**, 150.
10. I. J. Ferguson, A. R. Katritzky, and R. Patel, *J. Chem. Soc., Perkin Trans. 2,* **1976**, 1564.
11. T. Okawara, S. Ehara, M. Eto, K. Harano, and M. Furukawa, *Tetrahedron Lett.*, 1993, **34**, 4231.
12. T. Okawara, K. Uchiyama, Y. Okamoto, T. Yamasaki, and M. Furukawa, *J. Chem. Soc., Chem. Commun.*, **1990**, 1385.
13. T. Okawara, S. Ehara, S. Matsumoto, Y. Okamoto, T. Yamasaki, and M. Furukawa, *J. Chem. Soc., Perkin Trans. I,* **1990**, 2615.
14. A. R. Katritzky and W. Q. Fan, *J. Org. Chem.*, 1990, **55**, 3205.
15. A. R. Katritzky, W. Q. Fan, and C. Fu, *J. Org. Chem.*, 1990, **55**, 3209.
16. A. R. Katritzky, L. Urogdi, and A. Mayence, *J. Chem. Soc., Chem. Commun.*, **1989**, 337.
17. G. R. Weisman, V. Johnson, and R. E. Fiala, *Tetrahedron Lett.*, 1980, **21**, 3635.
18. D. S. Black, D. C. Craig, O. Giitsidis, R. W. Read, A. Salek, and M. A. Sefton, *J. Org. Chem.*, 1991, **56**, 4308.
19. H. Yamamoto and K. Maruoka, *J. Am. Chem. Soc.*, 1981, **103**, 4186.

Received, 9th January, 1995