Fused *s*-Triazino Heterocycles. XIII. 1,3,7,10,11c-Pentaazabenz[*de*]-anthracene and 1,3,7,10,11,13,13d-Heptaazabenz[*de*]cyclopenta[*h*]-anthracene, Two New Ring Systems

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The synthesis of the title compounds **5a-c** and **6a-c** is described using, 2,6-diaminopyridine as starting material. The key intermediates are 2-*t*-butyl-4-cyano-5(2-dimethylaminoethenyl)-1,3,6,9b-tetraazaphenalene **4** and 10-amino-2-*t*-butyl-10,11-dihydro-11-imino-1,3,7,10,11c-pentaazabenz[*de*]anthracene **5c**.

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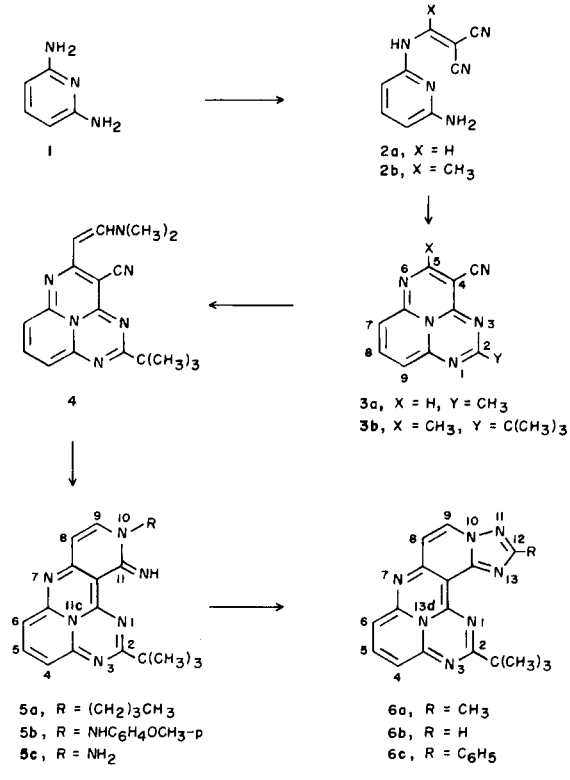
A known synthesis [2] of the 1,3,6,9b-tetraazaphenalene ring system **3** provides a cyano group at position-4 of **3**. This synthesis involved first reacting ethoxymethylenemalononitrile (**7**) with 2,6-diaminopyridine (**1**) to give 3-*N*-(6-amino-2-pyridyl)amino-2-cyanopropenenitrile (**2a**) and then closing the ring with acetic anhydride affording 4-cyano-2-methyl-1,3,6,9b-tetraazaphenalene (**3a**). The construction of the title ring systems **5** and **6** sought to utilize this cyano group in a ring closure reaction. A methyl group was needed at position-5 of **3**. This was accomplished by substituting (1-ethoxyethylidene)malononitrile for **7** in the before mentioned 2,6-diaminopyridine reaction giving 3-*N*-(6-amino-2-pyridyl)amino-2-cyano-2-butenenitrile (**2b**) in 58% yield. The reaction of **2b** with trimethylacetyl chloride in the presence of pyridine gave a 31% yield of 2-*t*-butyl-4-cyano-5-methyl-1,3,6,9b-tetraazaphenalene (**3b**). The *t*-butyl group at position-2 of **3b** served to limit the reaction of *N,N*-dimethylformamide diethyl acetal (**8**) (used in the next step) to the methyl group at position-5 of **3b**. Thus refluxing **3b** with **8** in toluene for 8 hours gave 2-*t*-butyl-4-cyano-5-(2-dimethylaminoethenyl)-1,3,6,9b-tetraazaphenalene (**4**) in 34% yield. The ring closure was completed by refluxing **4** with an aliphatic amine, *n*-butylamine in toluene for 42 hours to give 10-butyl-2-*t*-butyl-10,11-dihydro-11-imino-1,3,7,10,11c-pentaazabenz[*de*]-anthracene (**5a**) in 13% yield. The proposed structure of **5a** is supported by elemental analysis, ir and pmr spectra. The ir absorption at 4.5 μ (CN) and the pmr six-proton singlet (δ 3.05, $(CH_3)_2$ NH) both present in **4** are absent in **5a**. Further **5a** shows an ir absorption at 3.00 μ (NH) and appropriate pmr signals for the remaining hydrogens. Similarly, **4** was refluxed for 48 hours with an aromatic amine, *p*-anisidine, in the presence of 4-dimethylaminopyridine as catalyst, and gave a 74% yield of 2-*t*-butyl-10-(4-methoxyphenyl)-10,11-dihydro-11-imino-1,3,7,10,-11c-pentaazabenz[*de*]anthracene (**5b**).

Use of hydrazine monohydrate (**9**) to effect ring closure of **4** afforded 10-amino-2-*t*-butyl-10,11-dihydro-11,imino-1,3,7,10,11c-pentaazabenz[*de*]anthracene (**5c**), a compound which later proved capable of further ring closure. Thus refluxing **5c** with acetic anhydride for 21 hours gave a 63% yield of 2-*t*-butyl-12-methyl-1,3,7,10,11,13,13d-heptaazabenz[*de*]cyclopenta[*h*]anthracene (**6a**). The structure of **6a** was supported by a satisfactory elemental analysis, the absence of any NH-absorption in the ir, the presence of a pmr three-proton singlet (δ 2.56, CH_3 at position-12) and appropriate pmr signals for the remaining hydrogens. A similar reaction of **5c** with triethyl orthoformate and benzoic anhydride gave 2-*t*-butyl-1,3,7,10,11,13,13d-heptaazabenz[*de*]cyclopenta[*h*]anthracene (**6b**) and 2-*t*-butyl-12-phenyl-1,3,7,10,11,13,13d-heptaazabenz[*de*]cyclopenta[*h*]-anthracene (**6c**) in 61% and 28% yields respectively.



We are currently investigating the generality of the ring closure reaction sequence developed in this paper on some simpler substrates, that is reaction of an α-methyl-β-cyano nitrogen heterocycle with **8** followed by **9** and then final ring closure with an acylating agent.

EXPERIMENTAL

Melting points were determined in open capillaries on a Thomas-Hoover melting point bath and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 735B spectrophotomer. The pmr spectra were determined on a Varian EM-360 spectrometer using TMS as an internal reference. Analyses were performed by Micro-Analysis Inc., Wilmington, Delaware. All evaporations were carried out on a rotary evaporator at reduced pressure.

Pyridine, 1,2-dimethoxyethane (glyme), and toluene were dried using standard methods and stored over molecular sieves. Silica gel (70-230 mesh) for column chromatography was obtained from ICN Pharmaceutical Inc. Trimethylacetyl chloride, *N,N*-dimethylformamide diethyl acetal, 2,6-diaminopyridine, 4-dimethylaminopyridine, and (1-ethoxyethylidene)malononitrile were purchased from Aldrich Chemical Company and were used without further purification.

3*N*-(6-Amino-2-pyridyl)amino-2-cyano-2-butenenitrile (**2b**).

A solution of 13.5 g (0.12 mole) of 2,6-diaminopyridine, 16.8 g (0.12 mole) of (1-ethoxyethylidene)malonitrile and 150 ml of ethanol was refluxed for 2 hours. The precipitate which formed on cooling the reaction mixture in an ice bath was filtered and washed with ether, 13.9 g (58%), mp 209-211°. Recrystallization from ethanol gave white crystals, mp 210-211°; ir λ (Nujol): μ 2.98, 3.02 (NH), 4.5 (CN); pmr (DMSO-d_6): δ 2.37 (s, 3H, CH_3), 6.28 [d (J = 8 Hz), 1H, H_3 or H_5], 6.41 [d (J = 8 Hz), 1H, H_3 or H_5], 7.39 [t, J = 8 Hz), 1H, H_4].

Anal. Calcd. for $C_{10}H_9N_5$: C, 60.29; H, 4.55; N, 35.16. Found: C, 60.05; H, 4.74; N, 35.42.

2-*t*-Butyl-4-cyano-5-methyl-1,3,6,9b-tetraazaphenalene (**3b**).

A cold (0-5°) stirred slurry of 3.98 g (0.02 mole) of **2b**, 1.58 g (0.02 mole) of dry pyridine and 31 ml of dry glyme (nitrogen atmosphere) was treated dropwise with 5.79 g (0.048 mole) of trimethylacetyl chloride while maintaining the temperature at/or slightly below 5° during the addition. The mixture was allowed to warm to 15°, then gently refluxed for 3 hours, cooled to room temperature, filtered and the filter cake was washed several times with ether. A cold (−3-0°) stirred slurry of the reaction product in 15 ml of methanol was carefully neutralized to *p*H 8 by the dropwise addition of 5% methanolic sodium methoxide. The precipitate that formed was collected by filtration, washed several times with ether, then extracted with 60 ml of boiling chloroform. Evaporation of the extract to dryness gave a purple solid, 1.65 g (31%) mp 256-259°. Recrystallization from 2-ethoxyethanol gave beautiful violet shimmering plates, mp 261-262°; ir λ (Nujol): μ 4.59 (CN); pmr (deuteriochloroform): δ 1.15 [s, 9H, $(CH_3)_3C$], 2.09 (s, 3H, CH_3), 5.99 (m, 2H, H_7, H_9), 7.18 [t, (J = 8 Hz), 1H, H_8].

Anal. Calcd. for $C_{15}H_{15}N_5$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.72; H, 5.70; N, 26.68.

2-*t*-Butyl-4-cyano-5-(2-dimethylaminoethenyl)-1,3,6,9b-tetraazaphenalene (**4**).

A solution of 0.56 g (0.0021 mole) of **3b**, 0.618 g (0.0042 mole) of *N,N*-dimethylformamide diethyl acetal and 5 ml of dry toluene was refluxed for 8 hours. The precipitate that formed on cooling to room temperature was collected by filtration and washed several times with small amounts of ether, 0.23 g (34%), mp 235-239°. Recrystallization from carbon tetrachloride gave dull purple crystals, mp 235-236°; ir λ (Nujol): μ 4.50 (CN); pmr (deuteriochloroform): δ 1.2 [s, 9H, $(CH_3)_3C$], 3.05 [s, 6H, $(CH_3)_2N$], 5.12 [d (J = 12 Hz), 1H, C=CH], 5.76 (m, 1H, H_7 or H_9), 6.02 (m, 1H, H_7 or H_9), 7.10 [t, (J = 8 Hz), 1H, H_8], 7.88 [d (J = 12 Hz), 1H, C=CH].

Anal. Calcd. for $C_{18}H_{20}N_6$: C, 67.47; H, 6.29; N, 26.23. Found: C, 67.21; H, 5.99; N, 26.41.

10-Butyl-2-*t*-butyl-10,11-dihydro-11-imino-1,3,7,10,11c-pentaazabenz[*de*]-anthracene (**5a**).

A solution of 2.4 g (0.0075 mole) of **4**, 3.55 g of dry *n*-butylamine (0.048 mole) and 12 ml of dry toluene was refluxed for 42 hours and then evaporated to dryness. The residue was heated to boiling with 50 ml of petroleum ether (100-115°) and filtered; the filtrate was evaporated to dryness. The residue was chromatographed over 28 g of alumina using first methylene chloride to remove several trace unidentified contaminants (blue and green) and then chloroform-ethyl acetate (90/10) to collect crude **5a** as an amber fraction, 0.34 g (13%) mp 145-149°. Recrystallization from petroleum ether (100-115°) gave brown crystals mp 148-150°; ir λ (Nujol); μ 3.00 (NH), 4-5 transparent; pmr (deuteriochloroform): δ 0.85-1.55 [m, 16H, $(CH_3)_3C$ and $CH_3(CH_2)_2$], 3.38 [t, (J ~ 6 Hz), 2H, N-CH_2], 5.52 (m, 1H, H_4 or H_6), 5.82 [d (J = 6 Hz), 1H, H_8 or H_9], 6.00 (m, 1H, H_4 or H_6), 6.72 [t, (J = 6 Hz), 1H, H_5], 7.70 [d (J = 6 Hz), 1H, H_8 or H_9].

Anal. Calcd. for $C_{20}H_{24}N_6$: C, 68.94; H, 6.94; N, 24.12. Found: C, 68.88; H, 7.20; N, 24.40.

2-*t*-Butyl-10-(4-methoxyphenyl)-10,11-dihydro-11-imino-1,3,7,10,11c-pentaazabenz[*de*]anthracene (**5b**).

A solution of 1.00 g (0.0031 mole) of **4**, 2.46 g (0.02 mole) of *p*-anisidine, 2.44 g (0.02 mole) of 4-dimethylaminopyridine and 20 ml of dry toluene was refluxed for 48 hours. The precipitate that had formed was filtered and washed with petroleum ether (30-60°), 0.92 g (74%) mp 253-257°. Recrystallization from toluene gave brown fluffy crystals, mp 254-256°; ir λ (Nujol): μ 3.19 (NH); pmr (DMSO-d_6): δ 1.18 [s, 9H, $(CH_3)_3C$], 3.73 (s, 3H, CH_3O), 5.72 (m, 1H, H_4 or H_6), 6.00 [d (J = 6 Hz, 1H, H_8 or H_9], 6.09 (m, 1H, H_4 or H_6), 6.94 [d (J = 9 Hz), 2H, benzene H_3 and H_5], 7.14 [t, (J = 8 Hz), 1H, H_5], 7.51 [d (J = 9 Hz), 2H, benzene H_2 and H_6], 7.76 [d (J = 6 Hz), 1H, H_8 or H_9].

Anal. Calcd. for $C_{23}H_{22}N_6O$: C, 69.32; H, 5.57; N, 21.09. Found: C, 68.99; H, 5.60; N, 21.32.

10-Amino-2-*t*-butyl-10,11-dihydro-11-imino-1,3,7,10,11c-pentaazabenz-[*de*]anthracene (**5c**).

A stirred mixture of 1.00 g (0.0031 mole) of **4**, 0.16 g (0.0031 mole) of hydrazine monohydrate and 14 ml of toluene was refluxed for 1.25 hours and then filtered while still hot. The collected brown solid was washed with a little toluene and then with petroleum ether (30-60°) until the washings ran colorless. Recrystallization from toluene gave 0.36 g (36%) of **5c** as brown crystals, mp 261-262° dec; ir λ (Nujol): μ 3.13, 3.22, (NH); pmr (DMSO-d_6): δ 1.22 [s, 9H $(CH_3)_3C$], 6.11 [d (J ~ 8 Hz), 1H, H_8 or H_9], 6.26 [dd (J = 8,2 Hz), 1H, H_4 or H_6], 6.42 [dd (J = 8,2 Hz), 1H, H_4 or H_6], 7.62 [t (J = 8 Hz), 1H, H_5], 7.77 [d (J ~ 8 Hz), 1H, H_8 or H_9], 9.29 [s (broad), 2H, NH_2 exchangeable with deuterium oxide], 9.99 [s (broad), 1H, NH exchangeable with deuterium oxide].

Anal. Calcd. for $C_{17}H_{17}N_7$: C, 62.53; H, 5.57; N, 31.90. Found: C, 62.24; H, 5.73; N, 31.76.

2-*t*-Butyl-12-methyl-1,3,7,10,11,13,13d-heptaazabenz[*de*]cyclopenta[*h*]-anthracene (**6a**).

A stirred mixture of 0.61 g (0.002 mole) of **5c** and 8 ml of acetic anhydride was refluxed for 21 hours and filtered while still hot. The collected solid was washed with ether until the washings were pale yellow and then oven dried (100°), 0.42 g (63%) mp 271-274°. Column chromatography of this material (silica gel, 45 g, with methylene chloride: methanol/95:5) to remove a trace (tlc) but persistent impurity, followed by recrystallization from acetic anhydride gave the analytical sample, light green crystals, mp 270-272°; ir λ (Nujol): μ 2.5-3.2 no significant absorption; pmr (deuteriochloroform): δ 1.30 [s, 9H, $(CH_3)_3C$], 2.56 (s, 3H, CH_3), 5.76 [dd (J = 8,2 Hz), 1H, H_4 or H_6], 6.14 [dd (J = 8,2 Hz), 1H, H_4 or H_6], 6.40 [d (J = 6 Hz), 1H, H_8 or H_9], 7.11 [t (J = 8 Hz), 1H, H_5], 8.25 [d (J = 6 Hz), 1H, H_8 or H_9].

Anal. Calcd. for $C_{18}H_{17}N_7$: C, 65.24; H, 5.17; N, 29.58. Found: C, 65.46; H, 5.05; N, 29.29.

2-*t*-Butyl-1,3,7,10,11,13,13d-heptaazabenz[*de*]cyclopenta[*h*]anthracene (**6b**).

A stirred mixture of 0.61 g (0.002 mole) of **5c** and 25 ml of triethyl orthoformate was refluxed for 24 hours. The cooled slightly turbid solution was filtered to remove a trace of insoluble material and evaporated to dryness. The solid residue was washed with ether until the washings were almost colorless and then oven dried (100°), 0.39 g (61%), mp 223-227°. Recrystallization from toluene gave brownish-green crystals of **6b**, mp 226-227°; ir (Nujol): μ 2.5-3.2 no significant absorption; pmr (deuteriochloroform): δ 1.30 [s, 9H $(CH_3)_3C$], 5.80 [dd (J = 8,2 Hz), 1H, H_4 or H_6], 6.17 [dd (J = 8,2 Hz), 1H, H_4 or H_6], 6.46 [d (J = 6 Hz), 1H, H_8 or H_9], 7.13 [t (J = 8 Hz), 1H, H_5], 8.31 [d (J = 6 Hz), 1H, H_8 or H_9], 8.36 (s, overlaps part of doublet at 8.31, 1H, H_{12}).

Anal. Calcd. for $C_{17}H_{15}N_7$: C, 64.34; H, 4.76; N, 30.90. Found: C, 64.12; H, 5.02; N, 30.73.

2-*t*-Butyl-12-phenyl-1,3,7,10,11,13,13d-heptaazabenz[*de*]cyclopenta[*h*]-anthracene (**6c**).

A stirred solution of 0.61 g (0.002 mole) of **5c**, 0.90 g (0.004 mole) of benzoic anhydride and 5 ml of dry pyridine was refluxed for 24 hours. The cooled reaction mixture was filtered and the collected solid was washed with ether till the washings were colorless. Recrystallization from 2-methoxyethanol gave 0.22 g (28%) of **6c** as dark brown-green crystals, mp 273-274° dec; ir λ (Nujol): μ 2.5-3.2 no significant absorptions; pmr (deuteriochloroform): δ 1.31 [s, 9H $(CH_3)_3C$], 5.82 [dd (J = 8,2 Hz), 1H, H_4 or H_6], 6.20 [dd (J = 8,2 Hz), 1H, H_4 or H_6], 6.43 [d (J = 6 Hz), 1H, H_8 or H_9], 7.12 [t (J = 8 Hz), 1H, H_5], 7.44-8.52 (m, 6H, C_6H_5 and H_8 or H_9).

Anal. Calcd. for $C_{23}H_{19}N_7$: C, 70.21; H, 4.87; N, 24.91. Found: C, 69.93; H, 4.76; N, 24.76.

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REFERENCES AND NOTES

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