

Fused *s*-Triazino Heterocycles. XIV
 8*H*-1,3,7,8,9,10*c*-Hexaazacyclopenta[*a*]phenalene,
 1,3,7,8,10,11*c*-Hexaazabenz[*de*]anthracene and
 13*H*-4,6,8,13*a*,13*c*-Pentaazabenz[*de*]naphthacene,
 Three New Ring Systems

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The synthesis of the title compounds **3**, **4** and **5** is described, using 7,9-dibromo-5-tribromomethyl-2-*t*-butyl-4-cyano-1,3,6,9*b*-tetraazaphenalene **2a** as starting material. The key intermediates are 7,9-dibromo-2-*t*-butyl-4-cyano-5-hydrazino-1,3,6,9*b*-tetraazaphenalene **2b**, 5-benzamidino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9*b*-tetraazaphenalene **2c**, and 7,9-dibromo-2-*t*-butyl-5-(2-carboxyanilino)-4-cyano-1,3,6,9*b*-tetraazaphenalene **2e**.

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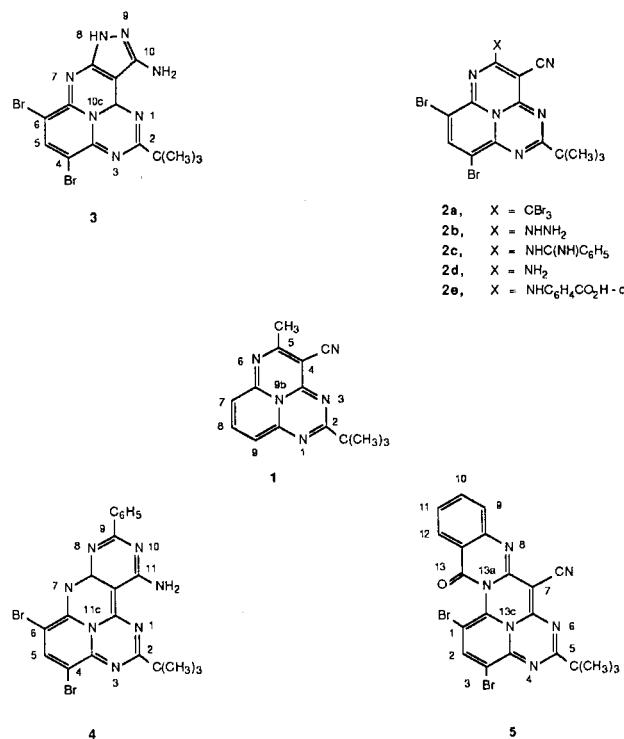
A recent paper [2] described the preparation of 1,3,7-, 10,11*c*-pentaazabenz[*de*]anthracene (**6**) and 1,3,7,10,11-, 13,13*d*-heptaazabenz[*de*]cyclopenta[*h*]anthracene (**7**), two new ring systems, using 2-*t*-butyl-4-cyano-5-methyl-1,3,6,9*b*-tetraazaphenalene (**1**) as starting material. In that paper, annulation reactions involving the adjacent methyl and cyano groups gave rise to **6** and **7**. In the present paper we show how 7,9-dibromo-5-tribromomethyl-2-*t*-butyl-4-cyano-1,3,6,9*b*-tetraazaphenalene (**2a**) served as starting material for additional annulation reactions leading to three new ring systems. Here suitable nucleophiles displaced the tribromomethyl group and then were caused to ring-close either on the neighboring cyano group or on the α -ring nitrogen. The synthesis of **2a** in 57% yield involved the base catalyzed (sodium acetate) bromination of **1**.

Several attempts to prepare 10-amino-4,6-dibromo-2-*t*-butyl-8*H*-1,3,7,8,9,10*c*-hexaazacyclopenta[*a*]phenalene (**3**) in one step from **2a** and hydrazine monohydrate resulted in a host of intractable products. A more satisfactory procedure consisted in first preparing 7,9-dibromo-2-*t*-butyl-4-cyano-5-hydrazino-1,3,6,9*b*-tetraazaphenalene (**2b**) (79%) by reacting **2a** with excess hydrazine monohydrate. Ring closure of **2b** to **3** in a subsequent step was accomplished by refluxing **2b** in chloroform for 3 hours in the presence of 4-dimethylaminopyridine, the latter serving to catalyze the ring closure. The structure [3] of **3** is supported by a satisfactory elemental analysis, the absence of any CN-absorption in the ir, and the presence of appropriate pmr signals.

A similar two-step procedure was used to prepare 11-amino-4,6-dibromo-2-*t*-butyl-9-phenyl-1,3,7,8,10,11*c*-hexaazabenz[*de*]anthracene (**4**). Thus reaction of excess benzamidino with **2a** gave 5-benzamidino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9*b*-tetraazaphenalene (**2c**) (36%). Refluxing **2c** in chlorobenzene together with 4-dimethylaminopyridine resulted in a 52% yield of **4**. The structure

[3] of **4** was supported by a satisfactory elemental analysis, the absence of any CN-absorption in the ir, and the presence of appropriate pmr signals. A small amount (4%) of what later proved to be 5-amino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9*b*-tetraazaphenalene (**2d**) was also formed in this ring-closure reaction. This by-product could have formed by loss of benzonitrile from the benzamidino-substituent of **2c**. An authentic sample of **2d** (72%) was prepared from **2a** and ammonia.

Figure 1



A displacement reaction by anthranilic acid on **2a** in the presence of triethylamine and 4-dimethylaminopyridine gave 7,9-dibromo-2-*t*-butyl-5-(2-carboxyanilino)-4-cyano-1,3,6,9b-tetraazaphenalene (**2e**) in 65% yield. Conversion of **2e** to 1,3-dibromo-5-*t*-butyl-13*H*-4,6,8,13a,13c-pentaaza-benzo[*de*]naphthacen-13-one (**5**) (43%) was accomplished by the cyclo-dehydration of **2e** using refluxing acetic anhydride as catalyst and dehydrating agent. Support for the structure of **5** was obtained by satisfactory elemental analysis, absence of any NH or OH absorption and presence of CN-absorption in the ir, appropriate pmr signals.

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 spectrophotometer. The pmr spectra were determined on a Varian EM360 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.

Silica gel (70-230 mesh) for column chromatography was obtained from ICN Pharmaceutical Inc.

7,9-Dibromo-5-tribromomethyl-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**2a**).

A stirred solution of 32.82 g (0.40 mole) of anhydrous sodium acetate and 10.61 g (0.04 mole) of 2-*t*-butyl-4-cyano-5-methyl-1,3,6,9b-tetraazaphenalene (**1**) [2] in 160 ml of acetic acid was treated dropwise at 75-80° with a solution of 32.82 g (0.40 mole) of bromine in 30 ml of acetic acid over a period of 45 minutes. The reaction mixture was stirred at 75-80° for an additional 8 hours, then cooled to room temperature and filtered. The filter cake was washed with petroleum ether (30-60°) until the washings were free of bromine. A solution of the crude product in 200 ml of toluene was filtered at the boil and the resulting filtrate was evaporated to dryness. The residue was digested in 700 ml of boiling carbon tetrachloride for one hour before being refrigerated overnight. The green crystals that formed were collected by vacuum filtration and were washed several times with petroleum ether (30-60°) before oven drying at 100°, 14.96 g (57%) mp 266-268° dec. Recrystallization from carbon tetrachloride did not alter the melting point; ir λ (Nujol): μm 4.55 (CN); pmr (deuteriochloroform): δ 1.21 (s, 9H, (CH₃)₃C), 7.79 (s, 1H, H₈).

Anal. Calcd. for C₁₅H₁₀Br₅N₅: C, 27.30; H, 1.53; N, 10.62. Found: C, 27.53; H, 1.38; N, 10.38.

7,9-Dibromo-2-*t*-butyl-4-cyano-5-hydrazino-1,3,6,9b-tetraazaphenalene (**2b**).

A stirred mixture of 4.5 g (0.091 mole) of hydrazine monohydrate and 60 ml of chloroform was treated dropwise at 3-5° with a solution of 6.0 g (0.0091 mole) of **2a** in 300 ml of chloroform over a period of 1 hour. Immediately upon completion of the addition, the mixture was filtered through a pad of filter agent, Celite. The filtrate was treated successively with 60 ml of 5% hydrochloric acid, 60 ml of 5% aqueous sodium bicarbonate, and 60 ml of saturated aqueous sodium chloride and then was evaporated to approximately one tenth volume and filtered. The filter cake was washed with carbon tetrachloride and oven dried at 100°, 3.15 g (79%), mp 243-245° dec. Recrystallization from chloroform-petroleum ether (60-90°) gave red fluffy crystals, mp 245-247° dec; ir λ (Nujol): μm 3.09 (broad, NH), 4.51 (CN); pmr (DMSO-*d*₆): δ 1.22 (s, 9H, (CH₃)₃C), 7.88 (s, 1H, H₈), 9.32 (br s, 3H, NHH₂).

Anal. Calcd. for C₁₄H₁₃Br₂N₇: C, 38.29; H, 2.98; N, 22.33. Found: C, 38.36; H, 3.21; N, 22.54.

10-Amino-4,6-dibromo-2-*t*-butyl-8*H*-1,3,7,8,9,10c-hexaazacyclopent[*a*]phenalene (**3**).

A stirred solution of 0.4 g (0.00091 mole) of **2b** and 1.22 g (0.01 mole) of 4-dimethylaminopyridine in 40 ml of chloroform was refluxed for 3 hours and filtered at the boil. The filter cake was washed with chloroform and oven dried at 100°, 0.18 g (45%) mp > 350°. Recrystallization from *o*-dichlorobenzene gave dull purple crystals, mp > 350°; tlc (silica gel/chloroform-methanol/9:1) showed one spot; ir λ (Nujol): μm 2.92, 3.01 (NH₂), 4-5 no significant absorption; pmr (DMSO-*d*₆): δ 1.23 (s, 9H, (CH₃)₃C), 8.03 (s, 1H, H₅), 9.89 (br s, 3H, NH₂, H₈).

Anal. Calcd. for C₁₄H₁₃Br₂N₇: C, 38.29; H, 2.98; N, 22.33. Found: C, 38.58; H, 3.09; N, 22.10.

5-Benzamidino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**2c**).

A stirred solution of 5.32 g (0.03 mole) of benzamidine hydrochloride was treated at 10° with 30 ml of a 1*N* methanolic solution of sodium methoxide. The mixture was stirred for several minutes, filtered and the filtrate was evaporated to give an oily residue. The residue was taken up with 20 ml of chloroform and filtered. The filtrate was treated dropwise at 4-5° with a solution of 2.0 g (0.003 mole) of **2a** in 100 ml of chloroform over a period of 1 hour. The precipitate which formed was stirred for an additional 30 minutes at 4-5°, filtered, and then was washed with chloroform. Recrystallization from chlorobenzene gave 0.57 g (36%) of green crystals, mp 325-328° dec; ir λ (Nujol): μm 2.92, 3.18 (NH), 4.49 (CN); pmr (DMSO-*d*₆): δ 1.13 (s, 9H, (CH₃)₃C), 7.35-7.94 (m, 5H, C₆H₅), 8.24 (s, 1H, H₈).

Anal. Calcd. for C₂₁H₁₇Br₂N₇: C, 47.84; H, 3.25; N, 18.60. Found: C, 47.99; H, 3.28; N, 18.36.

11-Amino-4,6-dibromo-2-*t*-butyl-9-phenyl-1,3,7,8,10,11c-hexaazabenz[*de*]anthracene (**4**) and 5-amino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**2d**).

A stirred solution of 0.4 g (0.00076 mole) of **2c**, 0.14 g (0.0011 mole) of 4-dimethylaminopyridine and 35 ml of chlorobenzene was refluxed for 24 hours and then evaporated to ~5 ml. The thin slurry was heated to boiling, filtered and the filtrate (Filtrate "A") was saved. The collected solid was washed several times with ether and then recrystallized from *N,N*-dimethylformamide (DMF) to give 0.17 g (42%) of **4**, brown crystals, mp 315-317°; ir λ (Nujol): μm 2.94, 3.22 (NH), 4-5 no significant absorption; pmr (DMSO-*d*₆): δ 1.30 (s, 9H, (CH₃)₃C), 7.51-8.35 (m, 5H, C₆H₅), 8.46 (s, 1H, H₈).

Anal. Calcd. for C₂₁H₁₇Br₂N₇: C, 47.84; H, 3.25; N, 18.60. Found: C, 47.62; H, 3.40; N, 18.61.

Filtrate "A" was evaporated to dryness and the residue was chromatographed over 65 g of silica gel using chloroform-methanol (96/4) as eluent. The first fraction (amber) yielded 0.09 g of crude **4**, mp 299-301°; recrystallization from DMF gave 0.04 g of **4**, mp 314-316° (52% combined yield). The second fraction (red) gave 0.045 g of crude **2d**, mp 248-250°. Recrystallization from 1-propanol gave 0.012 g (3%) of **2d**, red crystals, mp 284-285° dec, with ir and pmr spectra matching the sample of **2d** obtained by reaction of **2a** with ammonia.

Preparation of **2d** from **2a** and Ammonia.

A gentle stream of ammonia gas was passed through a vigorously stirred solution of 1.0 g (0.0015 mole) of **2a** in 50 ml of chloroform for ~30 minutes; during this time the temperature rose from 26 to 30°. The solid that formed after the reaction stood for 24 hours at room temperature, was collected by vacuum filtration, washed several times with petroleum ether (30-60°) and oven dried at 100°, 0.46 g (72%), mp 280-281°. Recrystallization from 1-propanol gave red crystals of **2d**, mp 284-285° dec; ir λ (Nujol): μm 2.96, 3.08 (NH), 4.55 (CN); pmr (DMSO-*d*₆): δ 1.21 (s, 9H, (CH₃)₃C), 8.0 (br s, 2H, NH₂), 8.25 (s, 1H, H₈).

Anal. Calcd. for C₁₄H₁₂Br₂N₆: C, 39.65; H, 2.85; N, 19.82. Found: C, 39.42; H, 3.01; N, 20.04.

7,9-Dibromo-2-*t*-butyl-5-(2-carboxyanilino)-4-cyano-1,3,6,9b-tetraazaphen-
alene (**2e**).

A stirred solution of 4.0 g (0.0061 mole) of **2a** in 40.0 ml of dry DMF was treated at 60-65° with 4.15 g (0.030 mole) of anthranilic acid, 1.48 g (0.012 mole) of 4-dimethylaminopyridine, and 1.84 g (0.018 mole) of dry triethylamine. The reaction mixture was stirred for 24 hours at ~65°, then allowed to cool to room temperature, filtered, and the filter cake was washed with ether to give a dull red solid. This solid was stirred in 30 ml of 1*N* hydrochloric acid for 45 minutes, filtered, washed with water and air dried, 2.15 g (65%), mp 318-321°. Recrystallization from DMF gave light blue crystals, mp 325-327° dec; ir λ (Nujol): μm 2.95-4.92 broad (OH), 4.55 (CN), 5.95 (CO); pmr (low solubility precluded pmr analysis).

Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{Br}_2\text{N}_6\text{O}_2$: C, 46.34; H, 2.96; N, 15.44. Found: C, 46.51; H, 3.05; N, 15.72.

1,3-Dibromo-5-*t*-butyl-13*H*-4,6,8,13a,13c-pentaazabenzode[naphthacen-
13-one (**5**).

A stirred solution of 0.5 g (0.00092 mole) of **2e** in 5 ml (0.053 mole) of acetic anhydride was refluxed for 21 hours and filtered at the boil. The filter cake was washed with ether, 0.21 g (43%), mp 328-332° dec.

Recrystallization from chlorobenzene gave rust-red crystals of **5**, mp 337-339° dec; ir λ (Nujol): μm 2.5-3.2 no significant absorption, 4.49 (CN), 5.89 (C=O); pmr (DMSO- d_6): δ 1.32 (s, 9H, (CH₃)₃C), 7.41-8.36 (m, 4H, H₉, H₁₀, H₁₁, H₁₂), 9.29 (s, 1H, H₂).

Anal. Calcd. for $\text{C}_{21}\text{H}_{14}\text{Br}_2\text{N}_6\text{O}$: C, 47.93; H, 2.68; N, 15.97. Found: C, 48.04; H, 2.61; N, 15.87.

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REFERENCES AND NOTES

- [1] Petroleum Research Fund Undergraduate Research Participant.
- [2] J. T. Shaw, G. F. Acciai, J. E. Babin and L. A. Sensenig, *J. Heterocyclic Chem.*, **23**, 381 (1986).
- [3] Tautomeric structures other than the one shown are also possible.