Fused *s*-Triazino Heterocycles. **XVI.** 13*H*-1,3,7,8,12a,13c-Hexaazabenzo[*de*]naphthacene and 1,3,7,8,11b,12,14,14d-Octaazadibenzo[*de,hi*]naphthacene, Two New Ring Systems

John T. Shaw*, Mallory F. Egler, Victoria S. Peciulis,

Regina Pustover and William G. Ruth

Department of Chemistry, Grove City College,
Grove City, PA 16127
Received January 26, 1990

The reaction of 7,9-dibromo-5-tribromomethyl-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**1a**) with 2-amino-5-picoline is shown to give 4,6-dibromo-2-*t*-butyl-13-imino-11-methyl-13*H*-1,3,7,8,12a,13c-hexaazabenzo[*de*]naphthacene (**3**) and the isomeric 7,9-dibromo-2-*t*-butyl-4-cyano-5*N*-(5-methyl-2-pyridyl)amino-1,3,-6,9b-tetraazaphenalene (**2a**). A related annulation reaction of 7,9-dibromo-2-*t*-butyl-5-chloro-4-cyano-1,3,6,9b-tetraazaphenalene (**1g**) with 2-amino-6-trimethylacetamidopyridine leads in two steps to 4,6-dibromo-2,13-di-*t*-butyl-1,3,7,8,11b,12,14,14d-octaazadibenzo[*de,hi*]naphthacene (**4a**). The preparation of **1g**, 5-azido-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**1c**) and the reaction of the latter with pyrrolidine leading to 7,9-dibromo-2-*t*-butyl-4-cyano-5-(1-pyrrolidino)-1,3,6,9b-tetraazaphenalene (**1e**) are also reported. Attempted displacement of the azido-group on **1c** by 2,6-diaminopyridine affords surprisingly 5-amino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**1d**).

An earlier paper [1] described the preparation of several new ring systems using 7,9-dibromo-5-tribromomethyl-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**1a**) as starting material. In that paper, suitable bidentate nucleophiles such as hydrazine or benzamidine first displaced the tribromomethyl group and then subsequently in an annulation reaction were allowed to close on the neighboring nitrile group to form a ring. This final reaction was catalyzed by 4-dimethylaminopyridine (**5**). In the present paper we describe the use of cyclic bi- and tridentate nucleophiles which then allow two or three rings to be fused on to **1**.
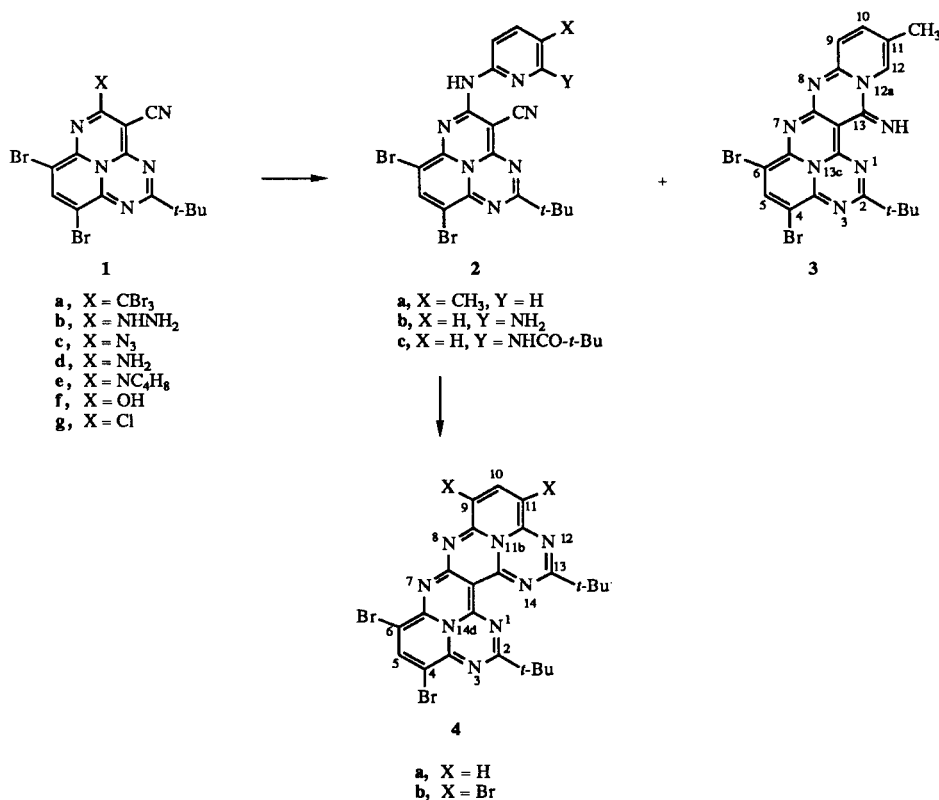
Previous work [1,2] had shown that while the tribromomethyl group is easily displaced by primary and secondary aliphatic amines, the displacement by aromatic amines requires catalysis by **5**. With this in mind, attempts were made to prepare 7,9-dibromo-2-*t*-butyl-4-cyano-5-*N*-(2-pyridyl)amino-1,3,6,9b-tetraazaphenalene by reacting **1a** with 2-aminopyridine in the presence of **5**. None of the reactions gave the desired compound, but instead gave unreacted **1a** or intractible materials depending on the severity of the reaction conditions. The use of an activated 2-aminopyridine proved a little more promising. Thus the **5**-catalyzed reaction of **1a** with 2-amino-5-picoline in refluxing chloroform for 21 hours gave not only 7,9-dibromo-2-*t*-butyl-4-cyano-5-*N*-(5-methyl-2-pyridyl)amino-1,3,6,9b-tetraazaphenalene (**2a**), (8%), but also 4,6-dibromo-2-*t*-butyl-13-imino-11-methyl-13*H*-1,3,7,8,12a,13c-hexaazabenzo[*de*]naphthacene (**3**), (9%). Column chromatography was used separate **2a** from **3**. Not surprisingly, recrystallization of either pure **2a** or **3** caused some equilibration resulting in a product slightly contaminated by the other isomer. The structures of **2a** and **3** were supported by satisfactory

elemental analyses and in the case of **2a** by the presence of CN and NH-absorption in the ir and appropriate pmr signals; by comparison **3** showed no CN-absorption but did give NH-absorption in the ir and suitable pmr signals.

An interesting possibility for further annulation reactions suggested itself if 2,6-diaminopyridine (**6**) were used in the displacement reaction with **1a**. That is, products analogous to **2a** or **3** could form, either of which might undergo ring closure with suitable acylating agents to form ring system **4**. Considerable effort was made to promote the reaction of **1a** with **6**, all unfruitful. The products were intractible tars. We were also unable to get 2-acetamido-6-aminopyridine to react with **1a**.

To further pursue the reaction of **6** with a suitable derivative of **1**, the use of the azido-group as leaving group was investigated. The preparation of 5-azido-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**1c**), (55%) involved the treatment of 7,9-dibromo-2-*t*-butyl-4-cyano-5-hydrazino-1,3,6,9b-tetraazaphenalene (**1b**) [1] with cold nitrous acid. The **5**-catalyzed reaction of **6** with **1c** in refluxing chloroform gave none of the desired 5-*N*-(6-amino-2-pyridyl)amino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**2b**) or its ring closed counterpart analogous to **3**. Instead a low yield (13%) 5-amino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**1d**) was isolated. Apparently **1d** was formed by thermal decomposition of **1c** to a nitrene followed by hydrogen abstraction. With the azide **1c** in hand, we were curious to see if a stronger nucleophile would displace the azide group. Addition of pyrrolidine to **1c** in chloroform at room temperature followed by a short reflux period resulted in a 38% yield of 7,9-dibromo-2-*t*-butyl-4-cyano-5-(1-pyrrolidino)-1,3,6,9b-tetraazaphenalene (**1e**). The structure of **1e** was

Scheme I

1

a, X = CBr₃
b, X = NHNH₂
c, X = N₃
d, X = NH₂
e, X = NC₄H₈
f, X = OH
g, X = Cl

2

a, X = CH₃, Y = H
b, X = H, Y = NH₂
c, X = H, Y = NHCO-t-Bu

3

4

a, X = H
b, X = Br

supported by satisfactory elemental analysis, absence of N₃ absorption but the presence of CN absorption in the ir and appropriate pmr signals. Further support for structure of **1e** was obtained by an independent synthesis of **1e** from **1a** and pyrrolidine.

An ideal leaving group at position-5 in **1** would of course be chloride. However, earlier unsuccessful efforts [2] to introduce this group into the 2 or 5-position of the 1,3,4,6,-9b-pentaazaphenalene ring-system was the major impetus that led to the developmet of the trichloromethyl leaving group for that system, and somewhat later [1] to the tribromomethyl group into the 5-position of **1**. Since the actual moiety that would bear the chlorine in the latter case is a pyrimidine ring rather than an *s*-triazine ring, it seemed worthwhile looking at this strategy again.

The introduction of chlorine into position-5 of **1** was accomplished by first hydrolyzing **1a** to 7,9-dibromo-2-*t*-butyl-4-cyano-5,6-dihydro-5-oxo-1,3,6,9b-tetraazaphenalene (**1f**) [3], (77% yield), using a solution of 1N aqueous hydrochloric acid in pyridine at 65° for 5 hours. Refluxing **1f** in phosphorus oxychloride for 1 hour gave 7,9-dibromo-2-*t*-butyl-5-chloro-4-cyano-1,3,6,9b-tetraazaphenalene (**1g**) in 76% yield. The preparation of **1g** is in itself a most interesting result as it represents the first halogen derivative of any 9b-azaphenalene ring system where the halogen is alpha to a ring nitrogen.

Reaction of **1g** with excess **6** in refluxing chloroform for 6 hours gave a 36% yield of **2b**; no catalysis by **5** was required. In the hope of making a derivative of **4** that would have reasonable solvent solubility so as to aid in its characterization, the double ring closure of **2b** to 4,6-dibromo-2,13-di-*t*-butyl-1,3,7,8,11b,12,14,14d-octaazadibenzo[*de,-hi*]naphthacene (**4a**) was attempted using trimethylacetic anhydride. This would provide a *t*-butyl-group at position-13 of **4**. The many products obtained from this reaction had such similar physical properties that separation was precluded. An alternative strategy using **1g** and 2-amino-6-trimethylacetamidopyridine (**7**) proved more advantageous. Thus refluxing **1g** with **7** in chlorobenzene for 8 hours gave a 33% yield of 7,9-dibromo-2-*t*-butyl-4-cyano-5-*N*-(6-trimethylacetamido-2-pyridyl)amino-1,3,6,9b-tetraazaphenalene (**2c**); catalysis by **5** was not required. The double ring-closure of **2c** to **4a** in 64% yield was accomplished by heating **2c** with *p*-toluenesulfonic acid in chlorobenzene for 40 minutes at 120°. The structure of **4a** was supported by satisfactory elemental analysis, the absence of CN, CO, and NH absorptions in the ir and appropriate pmr signals for the two *t*-butyl groups and the 4 peripheral hydrogens. Addition of bromine to a solution of **4a** in acetic acid containing sodium acetate gave symmetric 4,6,9,-11-tetrabromo-2,13-di-*t*-butyl-1,3,7,8,11b,12,14,14d-octaazadibenzo[*de,hi*]naphthacene (**4b**) in 25% yield. In addi-

tion to a satisfactory elemental analysis, **4b** had the required pmr spectrum: an eighteen-proton singlet for the two *t*-butyl groups and a two proton-singlet for protons H_5 and H_{10}.

The preparation of **7** in 46% yield involved the addition of trimethylacetyl chloride (1 mole) to **6** (2 mole) in dioxane at room temperature.

EXPERIMENTAL

Melting points were determined in open capillaries on a Thomas-Hoover melting point bath and are uncorrected. Infrared spectra were recorded on a Perkin Elmer-1600 spectrophotometer. The pmr spectra were determined on a Varian EM-360 spectrometer using TMS as an internal reference. Analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee. 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. 2-Amino-5-picoline and 4-dimethylaminopyridine were purchased from Aldrich Chemical Company.

7,9-Dibromo-2-*t*-butyl-4-cyano-5*N*-(5-methyl-2-pyridyl)amino-1,3,-6,9b-tetraazaphenalene (**2a**) and 4,6-Dibromo-2-*t*-butyl-13-imino-11-methyl-13*H*-1,3,7,8,12a,13c-hexaazabenzo[*de*]naphthacene (**3**).

A stirred mixture of 2.00 g (0.003 mole) of **1a** [1], 0.79 g (0.0073 mole) of 2-amino-5-picoline, 0.37 g (0.003 mole) of **5** and 16 ml of chloroform were refluxed for 21 hours and filtered at the boil. The filtrate was evaporated to about 8 ml and chromatographed over 70 g of silica gel using chloroform-ethyl acetate (90/10).

The first fraction (blue) gave 0.36 g of crude **1a**.

The second fraction (purple) gave 0.12 g (7.7%) of **2a**, purple crystals (tlc showed one spot), mp >330°; ir (Nujol): 3367 (NH), 2232 (CN) cm⁻¹; pmr (deuteriomethylene chloride): δ 1.26 (s, 9H, *t*-Bu), 2.30 (s, 3H, CH₃), 7.55 (dd, J = 8.91 and 2.10 Hz, 1H, pyridine H₄), 7.89 (s, 1H, H₈), 8.12 (br s, 1H, pyridine H₆), 8.33 (d, J = 8.91 Hz, 1H, pyridine H₃). This chromatographic sample was used for the elemental analysis as recrystallization from 2-methoxyethanol gave fine purple needles that were contaminated with **3** (tlc).

Anal. Calcd. for $C_{20}H_{17}Br_2N_7$ (**2a**): C, 46.62; H, 3.32; N, 19.03. Found: C, 46.81; H, 3.31; N, 18.81.

The third fraction (amber) gave 0.18 g of **3** that was slightly contaminated with **2a**. The crude was chromatographed again over 20 g of silica gel using the same eluent and gave 0.14 g (9.1%) of **3**, brown crystals (tlc showed one spot), mp >330°; ir (Nujol): 3125 (NH), 2500-2200 (transparent) cm⁻¹; pmr (deuteriomethylene chloride): δ 1.27 (s, 9H, *t*-Bu), 2.31 (s, 3H, CH₃), 7.17 (d, J = 8.90 Hz, 1H, H₉), 7.53 (dd, J = 8.90 and 2.10 Hz, 1H, H₁₀), 7.71 (s, 1H, H₅) 9.00 (br s, 1H, H₁₂). This sample was used for elemental analysis since recrystallization from toluene/hexane resulted in some of **3** equilibrating to **2a** (tlc).

Anal. Calcd. for $C_{20}H_{17}Br_2N_7$ (**3**): C, 46.62; H, 3.32; N, 19.03. Found: C, 46.75; H, 3.60; N, 18.75.

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

A thin slurry of 3.00 g (0.0068 mole) of 7,9-dibromo-2-*t*-butyl-4-cyano-5-hydrazino-1,3,6,9b-tetraazaphenalene (**1b**) and 48 ml of acetic acid was stirred for 5 minutes at room temperature; 30 ml of water was then added and the mixture was cooled to 10°. A solution 0.70 g (0.01 mole) of sodium nitrite in 6 ml of water was added dropwise. The mixture, which showed only a trace of starting material (tlc) after being stirred for 2 hours at 10-15°, was filtered and the filter cake was washed several times with water. The air-dried solid was chromatographed over 120 g of silica gel using chloroform-ethyl acetate (90/10) and gave 1.68 g (55%) of a dull-green solid. Recrystallization from carbon tetrachloride gave blue-green crystals, mp (the material turned brown at 183-185° with no further melting up to 300°); ir (Nujol): 2222 (CN), 2146 (N₃) cm⁻¹; pmr (DMSO-d₆): δ 1.15 (s, 9H, *t*-Bu), 8.38 (s, 1H, H₈).

Anal. Calcd. for $C_{14}H_{10}Br_2N_8$: C, 37.36; H, 2.24; N, 24.90. Found: C, 37.01; H, 2.16; N, 24.68.

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

A stirred mixture of 0.45 g (0.001 mole) of **1c**, 0.44 g (0.004 mole) of **6**, 0.37 g (0.003 mole) of **5** and 8 ml of chloroform was allowed to reflux for 43 hours and cooled to room temperature and filtered. The filtrate was chromatographed over 30 g of silica gel using chloroform-methanol (90/10) and gave 0.055 g (13%) of red crystals, mp 280-281°; ir (Nujol): 3378, 3225 (NH), 2211 (CN) cm⁻¹. The compound proved to be identical (mp, ir) to an authentic sample of **1d** obtained from the reaction of **1a** and ammonia [1].

Anal. Calcd. for $C_{14}H_{12}Br_2N_6$: C, 39.65; H, 2.85; N, 19.82. Found: C, 39.37; H, 2.65; N, 19.89.

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

From **1c**.

A stirred solution of 1.35 g (0.003 mole) of **1c** in 24 ml of chloroform was treated with 0.84 g (0.012 mole) of pyrrolidine at room temperature. The dark blue solution turned a purplish-red color immediately; only a trace of **1c** remained (tlc). The solution was then refluxed for 0.5 hours, chilled, and the red solid was collected by suction filtration and washed with petroleum ether (30-60°). Recrystallization from 2-methoxyethanol gave 0.54 g (38%) of red crystals, mp 304-305° dec; ir (Nujol): 2205 (CN) cm⁻¹; pmr (deuteriochloroform): δ 1.24 (s, 9H, *t*-Bu), 1.95 (m, 4H, CH₂CH₂), 3.88 (m, 4H, CH₂CH₂), 7.81 (s, 1H, H₈).

Anal. Calcd. for $C_{18}H_{18}Br_2N_6$: C, 45.21; H, 3.79; N, 17.58. Found: C, 45.00; H, 3.67; N, 17.48.

From **1a**.

A stirred solution of 1 g (0.0015 mole) of **1a** in 8 ml of chloroform was treated with 0.43 (0.006 mole) of pyrrolidine at room temperature. The blue solution turned purplish-red immediately. The remainder of the reaction and workup followed the procedure above (from **1c**): 0.59 g (82%) of red crystals, mp 304-305° dec; ir and pmr identical to **1e** prepared from **1c**.

7,9-dibromo-2-*t*-butyl-4-cyano-5,6-dihydro-5-oxo-1,3,6,9b-tetraazaphenalene (**1f**) [3].

A stirred solution of 9.9 g (0.015 mole) of **1a** in 75 ml of pyridine was treated with 15 ml of 1*N* hydrochloric acid at room temperature. The reaction mixture was then stirred at about 65° for 5 hours and then evaporated to dryness. The residue was stir-

red for 1 hour with 75 ml of ether, filtered and the collected solids were washed with ether until the washings were pale-blue. The oven-dried material (60°, 15 hours) was then stirred with a solution of 75 ml of distilled water and 30 ml of $1N$ hydrochloric acid for 0.5 hour and then oven dried (3 hours at 60° followed by 2 hours at 105°), 4.9 g (77%) mp 288-291° dec. This material was suitable for conversion to **1g**. The analytical sample was obtained by extracting the crude **1f** with a small amount of boiling chloroform-ethanol (80/20) and then recrystallizing the residue from 2-methoxyethanol; brownish-orange crystals, mp 320-321° dec; ir (Nujol): 2228 (CN), 1670 (C=O) cm^{-1}; pmr (DMSO-d$_6$): δ 1.24 (s, 9H, t-Bu), 8.50 (s, 1H, H$_8$).

Anal. Calcd. for $C_{14}H_{11}Br_2N_5O$: C, 39.55; H, 2.61; N, 16.48. Found: C, 39.28; H, 2.52; N, 16.21.

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

A stirred mixture of 4.8 g (0.011 mole) of **1f** and 70 ml of phosphorus oxychloride was refluxed for 1 hour. The residue from the evaporation of the reaction mixture was extracted with boiling carbon tetrachloride (3 x 80 ml). The combined extracts were filtered at the boil and then evaporated to dryness, 3.7 g (76%) of crude **1g**, mp 253-256°. This material was suitable for reaction with **6** and other nucleophiles. The analytical sample was obtained by column chromatography over silica gel using chloroform-ethyl acetate (95/5) followed by recrystallization from carbon tetrachloride, blue-black crystals, mp 259-261°; ir (Nujol): 2221 (CN) cm^{-1}; pmr (deuteriochloroform): δ 1.23 (s, 9H, t-Bu), 7.85 (s, 1H, H$_8$).

Anal. Calcd. for $C_{14}H_{10}Br_2ClN_5$: C, 37.91; H, 2.27; N, 15.79. Found: C, 37.63; H, 2.37; N, 15.77.

5-N-(6-Amino-2-pyridyl)amino-7,9-dibromo-2-t-butyl-4-cyano-1,3,-6,9b-tetraazaphenalene (2b).

A stirred mixture of 1.1 g (0.0025 mole) of **1g**, 1.09 g (0.01 mole) of **6** and 20 ml of chloroform was refluxed for 6 hours and filtered hot. The collected solids, after being washed with chloroform until the washings were colorless were allowed to air dry. They were then stirred with 33 ml of distilled water while the pH of the mixture was adjusted to about 10 with $1N$ sodium hydroxide. After being stirred for an additional 15 minutes, the suspended solids were collected, washed with small amounts of distilled water and then air dried. Recrystallization from N,N-dimethylformamide (DMF) gave 0.46 g (36%) of lavender crystals, mp 286-288° dec (rapid); ir (Nujol): 3454, 3389, 3341, 3216 (NH) 2206 (CN) cm^{-1}; pmr: very low solubility precluded analysis.

Anal. Calcd. for $C_{19}H_{16}Br_2N_8$: C, 44.20; H, 3.12; N, 21.71. Found: C, 44.04; H, 3.05; N, 21.48.

7,9-Dibromo-2-t-butyl-4-cyano-5-N-(6-trimethylacetamido-2-pyridyl)amino-1,3,6,9b-tetraazaphenalene (2c).

A stirred solution of 0.44 g (0.001 mole) of **1g**, 0.77 g (0.004 mole) of **7** and 8 ml of dry chlorobenzene was refluxed for 8 hours and then stirred for an additional 12 hours at room temperature. The mixture was chilled, filtered, and the filtrate was evaporated to dryness. The residue from the evaporation was stirred with 3 ml of methanol, filtered and the collected solids were washed with 1 ml portions of methanol until the washings were pale amber. Recrystallization of the dull purple solid from 2-methoxyethanol gave 0.2 g (33%) of purple crystals, mp 314-315° dec; ir (Nujol): 3433, 3385 (NH), 2206 (CN), 1689 (C=O) cm^{-1}; pmr (deuterio-

chloroform): δ 1.22 (s, 9H, t-Bu), 1.35 (s, 9H, t-Bu), 7.52-8.30 (m, 6H, (pyridine-H$_3$, H$_4$, H$_5$), two NH, and H$_8$).

Anal. Calcd. for $C_{24}H_{24}Br_2N_8O$: C, 48.01; H, 4.03; N, 18.67. Found: C, 48.17; H, 4.01; N, 18.62.

4,6-Dibromo-2,13-di-t-butyl-1,3,7,8,11b,12,14,14d-octaazadibenzo[de,hi]naphthacene (4a).

A stirred solution of 0.6 g (0.001 mole) of **4a** in 40 ml of chlorobenzene at about 120° was treated with 0.19 g (0.001 mole) of p-toluenesulfonic acid monohydrate. The solution was stirred for 40 minutes at 118-120° during which time a precipitate formed. The solids on cooling to room temperature were collected, washed successively with a little chlorobenzene and petroleum ether (30-60°). A stirred solution of the bronze-colored salt in 38 ml of methanol at about 45° was treated with 4 ml of pyridine. The precipitate that formed was allowed to stir at room temperature for 1 hour and then filtered and washed with methanol. Recrystallization from DMF gave 0.37 g (64%) of metallic-purple crystals, mp 318-320° dec; ir (Nujol): no significant absorption at 3500-3300, 2500-2000 and 1710-1640 cm^{-1}; pmr (deuteriochloroform): δ 1.28 (s, 9H, t-Bu), 1.30 (s, 9H, t-Bu), 6.20 (dd, J = 8 and 2 Hz, 1H, H$_9$ or H$_{11}$), 6.40 (dd, J = 8 and 2 Hz, 1H, H$_9$ or H$_{11}$), 7.29 (t, J = 8 Hz, 1H, H$_{10}$), 7.81 (s, 1H, H$_5$).

Anal. Calcd. for $C_{24}H_{22}Br_2N_8$: C, 49.50; H, 3.81; N, 19.25. Found: C, 49.56; H, 3.74; N, 19.35.

4,6,9,11-Tetrabromo-2,13-di-t-butyl-1,3,7,8,11b,12,14,14d-octaazadibenzo[de,hi]naphthacene (4b).

A stirred thin slurry of 0.21 g (0.0026 mole) of anhydrous sodium acetate and 0.5 g (0.00086 mole) of **4a** in 10 ml of acetic acid at about 75° was treated in small portions with 2.6 ml of $1M$ bromine (0.0026 mole) in acetic acid. The mixture was stirred at about 75° for 1 hour, filtered and the collected hydrobromide salt was washed well with ether. A stirred thin slurry of the purple salt in 35 ml of methanol became beige-colored on treatment with 4 ml of pyridine. The insoluble material was collected by suction filtration, and washed with methanol. Recrystallization from DMF gave 0.16 g (25% of dark brown crystals, mp >330°; pmr (deuteriochloroform): δ 1.22 (s, 18H, two t-Bu), 8.02 (s, 2H, H$_5$ and H$_{10}$).

Anal. Calcd. for $C_{24}H_{20}Br_4N_8$: C, 38.95; H, 2.72; N, 15.14. Found: C, 38.91; H, 2.69; N, 15.04.

2-Amino-6-trimethylacetamidopyridine (7).

A stirred solution of 21.82 g (0.2 mole) of **6** in 100 ml of dry dioxane was treated dropwise with a solution of 12.06 g (0.1 mole) of trimethylacetyl chloride in 16 ml of dry dioxane over a period of 50 minutes (nitrogen atmosphere) while maintaining the temperature at 25°. The mixture was stirred for an additional 2 hours, filtered and the filtrate was evaporated to dryness. The residue, a semi-solid, was stirred with 35 ml of water, filtered and the collected solids were washed well with water, then oven dried at 60° for 8 hours. Recrystallization from carbon tetrachloride gave 8.82 g (46%) of white crystals, mp 146-148°. Column chromatography over silica gel using chloroform-ethyl acetate (50/50) removed a trace impurity and gave the analytical sample mp 146-148°; ir (Nujol): 3475, 3370, 3294 (NH), 1660 (C=O) cm^{-1}; pmr (deuteriochloroform): δ 1.30 (s, 9H, t-Bu), 4.37 (br s, 2H, NH$_2$), 6.14 (dd, J = 8 and 2 Hz, 1H, H$_3$), 7.27-7.82 (m, 3H, H$_4$, H$_5$, NHC=O).

REFERENCES AND NOTES

[1] J. T. Shaw and M. C. Fair, *J. Heterocyclic Chem.*, **24**, 321 (1987).

[2] J. T. Shaw, T. W. Coffindaffer, J. B. Stimmel and P. M. Lindley, *ibid.*, **19**, 357 (1982).

[3] The structure of **1f** is represented in Scheme 1 as the 5-hydroxy tautomer for sake of convenience.