

Synthesis of 2,7-Disubstituted-4,5,9,10-tetraazapyrenes

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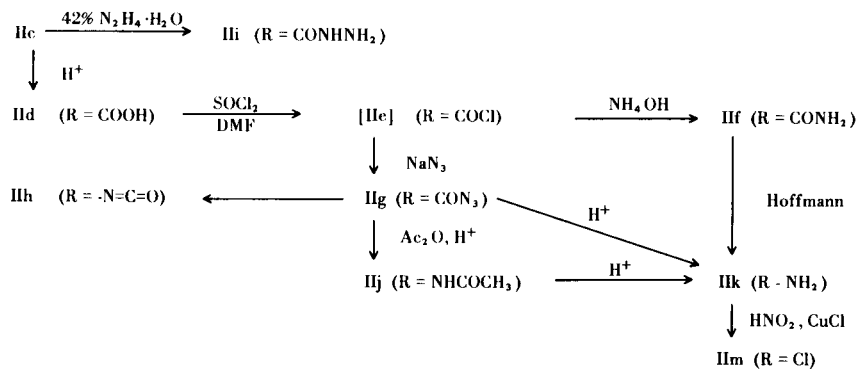
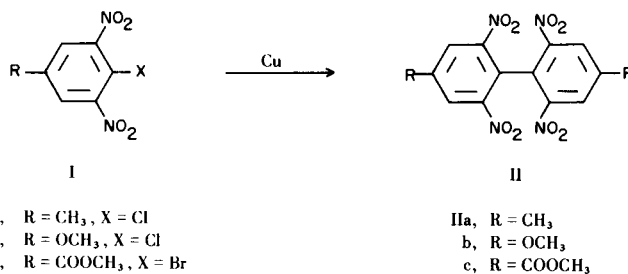
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2,7-Dimethyl-4,5,9,10-tetraazapyrene (VI) was synthesized by the catalytic hydrogenation of 4,4'-dimethyl-2,2',6,6'-tetranitrobiphenyl (IIa) with W-2 Raney nickel in the presence of alkali. 4,4'-Dicarbomethoxy-2,2',6,6'-tetranitrobiphenyl (IIc) under similar conditions in neutral medium gave 4,4'-dicarbomethoxy-2,2',6,6'-tetraaminobiphenyl (IV) which on oxidation gave 2,7-dicarbomethoxy-4,5,9,10-tetraazapyrene (V). 2,7-Dimethyl-, 2,7-dimethoxy-, and 2,7-diacetamido-4,5,9,10-tetraazapyrene di-*N*-oxides (III a,b,c) were obtained by catalytic reduction of the corresponding 4,4'-disubstituted-2,2',6,6'-tetranitrobiphenyls with W-7 Raney nickel in the presence of alkali. Compound VI on oxidation with hydrogen peroxide gave the di-*N*-oxide (IIIa).

Investigations in the 4,5,9,10-tetraazapyrene ring system have been limited. Stetter and Schwarz (1) first synthesized 4,5,9,10-tetraazapyrene by catalytic hydrogenation of 2,2',6,6'-tetranitrobiphenyl with Raney nickel in the presence of alkali. Holt and Hughes (2) synthesized the di-*N*-oxide of 4,5,9,10-tetraazapyrene by the oxidation of 1,10-diaminobenzo[*c*]cinnoline with peracetic acid. Furthermore, Holt and Hughes (2,3) reduced 4,5,9,10-tetraazapyrene di-*N*-oxide with stannous chloride to 4,5,

9,10-tetraazapyrene and confirmed its structure by re-oxidation to 4,5,9,10-tetraazapyrene di-*N*-oxide. The position of the two oxygen atoms in 4,5,9,10-tetraazapyrene di-*N*-oxide has not been conclusively proven but most probably it is 4,5,9,10-tetraazapyrene 4,9-dioxide.

Stille and his coworkers (4,5) have synthesized 1,2,3,6,7,8-hexahydro-4,5,9,10-tetraazapyrene and some of its derivatives by condensing 1,3-cyclohexanediones with excess hydrazine hydrate.



The purpose of this study was to synthesize the previously unknown 2,7-disubstituted-4,5,9,10-tetraazapyrenes and their di-*N*-oxides.

3,5-Dinitro-4-chlorotoluene (Ia) (6) has been synthesized previously from 4-methyl-2,6-dinitroaniline. We have prepared Ia from the known 4-methyl-2,6-dinitrophenol (7) by reaction with phosphorus oxychloride in the presence of pyridine. Compound Ia was allowed to react with copper powder in nitrobenzene to give 4,4'-dimethyl-2,2',6,6'-tetranitrobiphenyl (IIa). Similarly, 2,6-dinitro-4-methoxychlorobenzene (Ib) (8) gave 4,4'-dimethoxy-2,2',6,6'-tetranitrobiphenyl (IIb). 4,4'-Dicarbomethoxy-2,2',6,6'-tetranitrobiphenyl (IIc) had been prepared previously (9,10) from 2,6-dinitro-4-carbomethoxychlorobenzene; however, in our hands 2,6-dinitro-4-carbomethoxybromobenzene (Ic) gave a much better yield of IIc. Compound Ic was prepared by esterification of the known 3,5-dinitro-4-bromobenzoic acid (11).

Several methods were investigated for the preparation of 4,4'-diamino-2,2',6,6'-tetranitrobiphenyl (IIk). Selective reduction of 2,2',4,4',6,6'-hexanitrobiphenyl (9) with hydrogen sulfide in dioxane in the presence of ammonium hydroxide failed to give the desired diamine (IIk) as reported for 4-amino-2,6-dinitrotoluene from 2,4,6-trinitrotoluene (12,13).

Thus, it was necessary to prepare IIk by Hoffmann rearrangement of 2,2',6,6'-tetranitrobiphenyl-4,4'-dicarboxamide (IIf) or the Curtius rearrangement of the 2,2',6,6'-tetranitrobiphenyl-4,4'-dicarboxazide (IIg).

The dimethyl ester (IIc) was hydrolyzed under acidic or alkaline conditions to give 2,2',6,6'-tetranitrobiphenyl-4,4'-dicarboxylic acid (IIId) (10) which was converted to IIf by treatment with thionyl chloride in the presence of catalytic amounts of dimethylformamide (14) followed by treatment with ammonium hydroxide. The dicarboxamide (IIf) was rearranged to the diamine (IIk) under Hoffmann conditions (2,15) in variable yields (10-40%).

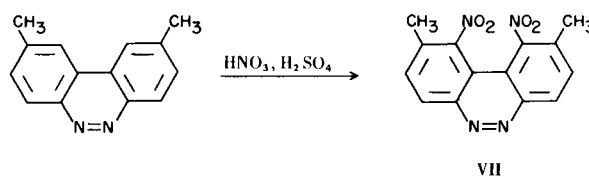
At first it appeared that the dicarboxazide (IIg) might be prepared easily from 2,2',6,6'-tetranitrobiphenyl-4,4'-dicarboxhydrazide (IIi). The reaction of the dimethyl ester (IIc) with 42% hydrazine hydrate in ethanol gave the dicarboxhydrazide (IIi) (16) in only poor yield. However, the dicarboxazide (IIg) was obtained in high yields from the 2,2',6,6'-tetranitrobiphenyl-4,4'-dicarbonyl chloride (IIe) by treatment with sodium azide (11) in acetic acid.

The dicarboxazide (IIg) was rearranged by heating with concentrated sulfuric acid (11) or by heating in toluene followed by treatment with concentrated hydrochloric acid (17) to give the diamine (IIk); however, the yields were poor (~20%). When sulfuric acid was used as the rearranging agent a compound of unknown structure was isolated as a major component.

The dicarboxazide (IIg) on heating with acetic anhydride

in the presence of a drop of concentrated sulfuric acid (11) gave 4,4'-diacetamido-2,2',6,6'-tetranitrobiphenyl (IIj) in good yield which upon acid hydrolysis gave the diamine (IIk). The diamine (IIk) on diazotization followed by treatment with cuprous chloride gave 4,4'-dichloro-2,2',6,6'-tetranitrobiphenyl (IIm).

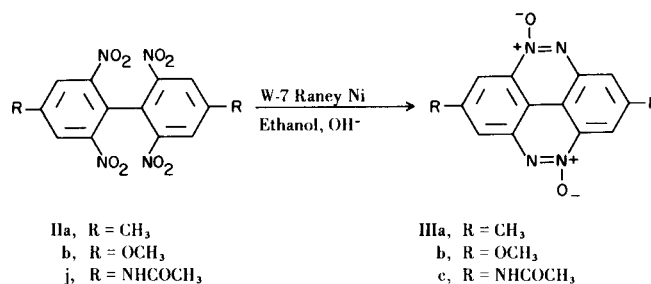
2,9-Dimethylbenzo[*c*]cinnoline (18) on nitration gave a dinitro compound to which we have assigned the structure 1,10-dinitro-2,9-dimethylbenzo[*c*]cinnoline (VII) on the basis of the NMR spectrum in deuteriochloroform; singlet, δ 2.81, (6H, two methyl groups); two doublets, δ 8.04 (2H) and δ 8.96 (2H) ($J = 8.5$ cps) assigned to 3,8 and 3,7 ring protons, respectively.



A similar situation has been observed in the nitration of benzo[*c*]cinnoline and 1-nitrobenzo[*c*]cinnoline where 1,10-dinitrobenzo[*c*]cinnoline has been obtained and characterized (19). 2,9-Dimethylbenzo[*c*]cinnoline 5-oxide has been reported to give 2,9-dimethyl-1-nitrobenzo[*c*]cinnoline 5-oxide (19).

Nitration of 4,5,9,10-tetraazapyrene (1) with a 1:1 mixture of concentrated sulfuric acid and concentrated nitric acid gave the starting material at room temperature while at 80° for 1 hour the starting material decomposed.

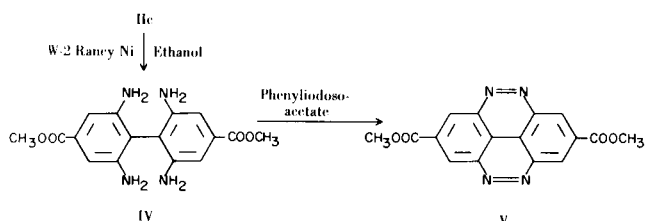
Catalytic reduction of 4,4'-dimethyl- (IIa), 4,4'-dimethoxy- (IIb), and 4,4'-diacetamido-2,2',6,6'-tetranitrobiphenyl (IIj) with W-7 Raney nickel in alcohol at atmospheric pressure in the presence of alkali gave the corresponding 2,7-disubstituted 4,5,9,10-tetraazapyrene di-*N*-oxides (III a,b,c). The structures of these dioxides have not been conclusively proven.



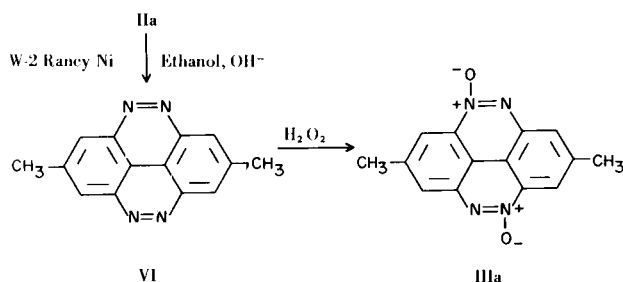
Under similar conditions the catalytic reduction of 4,4'-dicarbomethoxy- (IIc), 4,4'-dicarboxy- (IIId), 4,4'-diamino- (IIk), 4,4'-dichloro-2,2',6,6'-tetranitrobiphenyl

(II_m), 2,2',4,4',6,6'-hexanitrobiphenyl and 2,9-dimethyl-1,10-dinitrobenzo[*c*]cinnoline (VII), failed to give the corresponding tetraazapyrenes.

Compound II_c on catalytic reduction with W-2 Raney nickel in ethanol gave 4,4'-dicarbomethoxy-2,2',6,6'-tetraaminobiphenyl (IV) which on oxidation with phenyliodosoacetate (20) gave 2,7-dicarbomethoxy-4,5,9,10-tetraazapyrene (V).



Compound II_a on catalytic reduction with W-2 Raney nickel in the presence of alkali gave 2,7-dimethyl-4,5,9,10-tetraazapyrene (VI) which was oxidized to III_a with hydrogen peroxide in acetic acid. The constitution of III_a is assigned as the most likely structure but has not been unequivocally established.



EXPERIMENTAL

Melting points were taken on a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared, ultraviolet and nuclear magnetic resonance spectra were recorded on Perkin-Elmer 337, Cary-14, and Varian A-60 A spectrophotometers, respectively. The nuclear magnetic resonance spectra were compared with TMS as an internal standard or as an external standard whenever mentioned. DSS was used as an internal standard when deuterium oxide was the solvent.

3,5-Dinitro-4-chlorotoluene (I_a).

To 250 ml. of hot ethanol 51.4 g. (0.26 mole) of 4-methyl-2,6-dinitrophenol and 26.6 g. of pyridine were added and allowed to stand whereupon 56 g. (75%) of the pyridinium salt crystallized, m.p. 79-80°. The pyridinium salt (53 g.) was added to 200 ml. of phosphorus oxychloride and the mixture was refluxed for 2.5 hours. Since the reaction was not complete, 10 ml. of pyridine was added slowly and the mixture was refluxed for an additional 3 hours. The excess phosphorus oxychloride was removed *in vacuo*, the residue was poured on ice and extracted with chloroform. The chloroform extract after drying was evaporated to dryness and I_a

was recrystallized from ethanol, 21.5 g. (36%), m.p. 113° (lit. (6), 114°).

4-Carbomethoxy-2,6-dinitrobromobenzene (I_c).

3,5-Dinitro-4-bromobenzoic acid (10 g., 0.039 mole) was dissolved in 65 ml. of methanol, 4.5 ml. of concentrated sulfuric acid was added and the mixture was refluxed for 2 hours. The ester which crystallized on cooling was collected by filtration, washed with 50% aqueous methanol and dried in air to give 9.7 g. (92%) of I_c. The product was recrystallized from hexane, m.p. 116-118°; U.V. λ max (95% ethanol), 225 (ϵ , 32,920), 258 (sh) μ m (ϵ , 23,990).

Anal. Calcd. for C₈H₅BrN₂O₆: C, 31.50; H, 1.65; N, 9.19. Found: C, 31.45; H, 1.56; N, 9.05.

4,4'-Dimethyl-2,2',6,6'-tetranitrobiphenyl (II_a).

A mixture of 2 g. (0.00923 mole) of 3,5-dinitro-4-chlorotoluene (I_a), 2 g. of copper powder and 100 ml. of nitrobenzene was refluxed with stirring for 1 hour and then filtered hot. The residue was washed with 10 ml. of hot nitrobenzene and the filtrate was concentrated to about 25 ml. Ligroin (90-120° b.p.) (250 ml.) was added and upon chilling a pale yellow solid was deposited. This was collected, dried, and recrystallized from ethanol, yield 0.66 g. (40%), m.p. 250-252°; U.V. λ max (95% ethanol) 247 μ m (ϵ , 39,125); NMR (deuteriochloroform) δ 8.46 (singlet-4H, aromatic), δ 2.69 (singlet-6H, methyl).

Anal. Calcd. for C₁₄H₁₀N₄O₈: C, 46.41; H, 2.78; N, 15.47. Found: C, 46.16; H, 2.72; N, 15.43.

4,4'-Dimethoxy-2,2',6,6'-tetranitrobiphenyl (II_b).

2,6-Dinitro-4-methoxychlorobenzene (I_b) (8) (5 g., 0.0215 mole) was added to 50 ml. of nitrobenzene and the mixture was heated to 170°. Copper powder (4 g.) was added portionwise with stirring and the temperature of the reaction mixture was raised and maintained at 180-200° for 1 hour. The reaction mixture was cooled and filtered. The solvent was removed under reduced pressure and the residue was poured into 50 ml. of hexane. The crystals which separated on stirring were collected and recrystallized either from ethanol or benzene-hexane to give 3.8 g. (90%) of II_b, m.p. 200-202°; U.V. λ max (95% ethanol), 208 (ϵ , 71,030), 245 (sh) (ϵ , 27,120), 340 μ m (ϵ , 5,310); NMR (deuteriochloroform) δ 8.06 (singlet-4H, aromatic), δ 4.01 (singlet-6H, methyl).

Anal. Calcd. for C₁₄H₁₀N₄O₁₀: C, 42.65; H, 2.56; N, 14.20. Found: C, 42.90; H, 2.65; N, 14.21.

4,4'-Dicarbomethoxy-2,2',6,6'-tetranitrobiphenyl (II_c).

To 19 g. (0.0625 mole) of 2,6-dinitro-4-carbomethoxybromobenzene (I_c) was added 50 ml. of *p*-xylene, followed by addition of 4 g. of copper powder. The mixture was heated under reflux for 1 hour. After cooling, the reaction mixture was filtered and the filtrate was evaporated to dryness to give 11.1 g. (90%) of a brown residue which was recrystallized from ethanol-benzene, colorless crystalline flakes (charcoal), m.p. 171-172°. Occasionally another crystalline form (flat needles) m.p. 187-189° was obtained. Both crystalline forms exhibited the same NMR spectrum; (lit. (9), m.p. 173°; and lit. (10), 192-192.5°); U.V. λ max (95% ethanol), 220 μ m (ϵ , 33,860); NMR (deuteriochloroform), δ 9.35 (singlet-4H, aromatic), δ 4.2 (singlet-6H, methyl).

Anal. Calcd. for C₁₆H₁₀N₄O₁₂: C, 42.68; H, 2.31. Found: C, 42.68; H, 2.24.

2,2',6,6'-Tetranitrobiphenyl-4,4'-dicarboxylic Acid (II_d).

Fifteen g. (0.033 mole) of 4,4'-dicarbomethoxy-2,2',6,6'-tetranitrobiphenyl (II_c) was dissolved in 150 ml. of concentrated

sulfuric acid and water was added, dropwise with stirring until precipitation started. The mixture was heated for 1 hour on the steam bath, cooled and diluted with ice water to give a white product which was collected by filtration, washed with water and dried to give 12.2 g. (83%) of IId. The analytical sample was recrystallized from water after charcoal treatment, m.p. 350-352°, (lit. (10), 338-342°); NMR (sodium deuteroxide) δ 9.00 (singlet).

Anal. Calcd. for $C_{14}H_6N_4O_{12}$: C, 39.83; H, 1.43; N, 13.27. Found: C, 39.53; H, 1.65; N, 13.44.

2,2',6,6'-Tetranitrobiphenyl-4,4'-dicarboxamide (IIf).

To 25 ml. of thionyl chloride was added 2.11 g. (0.005 mole) of 2,2',6,6'-tetranitrobiphenyl-4,4'-dicarboxylic acid (IIId). To this suspension 2 drops of dimethylformamide were added and the mixture was refluxed with stirring for 30 minutes giving a clear solution. Excess thionyl chloride was removed *in vacuo* and the residue was dried in a vacuum desiccator overnight yielding a white powder (IIe). This was added to 50 ml. of cold 28% ammonium hydroxide whereupon the diamide precipitated. It was filtered, washed with water and dried to give 2.0 g. (95%) of IIf. Recrystallization from aqueous ethanol gave white crystals, m.p. 278-279°; U.V. λ max 217 μ (ϵ , 56,420).

Anal. Calcd. for $C_{14}H_8N_6O_{10}$: C, 40.00; H, 1.92; N, 19.99. Found: C, 39.96; H, 1.92; N, 20.01.

2,2',6,6'-Tetranitrobiphenyl-4,4'-dicarboxazide (IIg) and 2,2',6,6'-Tetranitrobiphenyl-4,4'-diisocyanate (IIh).

Ten and one half g. (0.025 mole) of 2,2',6,6'-tetranitrobiphenyl-4,4'-dicarboxylic acid (IIId) was added to 50 ml. of thionyl chloride. To this suspension 5 drops of dimethylformamide were added and refluxing with stirring for 30 minutes gave a clear solution. Excess thionyl chloride was removed *in vacuo* and the residue was dried in a vacuum desiccator overnight to give a white powder (IIe). This was suspended in 75 ml. of glacial acetic acid and 7 g. of sodium azide was added portionwise with stirring. The mixture was stirred for 30 minutes at room temperature, 200 ml. of water was added and stirring was continued an additional 15 minutes. The product was collected by filtration and dried at room temperature in a vacuum desiccator for 24 hours to give 10 g. (84%) of IIg. Pale yellow needles, m.p. 136-137° were obtained upon recrystallization from ether; NMR (deuterioacetone, external standard) δ 8.05 (singlet); infrared cm^{-1} : 3450(b), 3090(m), 2255(w), 2225(w), 2150(s), 1700(s), 1620(m), 1545(vs), 1450(w), 1340(s), 1305(w), 1270(vs), 1185(vs), 1125(w), 1060(w), 1005(w), 925(m), 838(w), 740(m), 725(m). The analytical sample on drying at 70° for 4 days *in vacuo* rearranged to the diisocyanate (IIh), yellow crystals, m.p. 166-167°; infrared cm^{-1} : 3400(b), 2300(s), 1770(w), 1700(w), 1510(s), 1430(m), 1350(w), 1330(w), 1275(w), 1185(m), 920(m), 895(w), 775(w), 725(m), 570(w).

Anal. Calcd. for (IIh) $C_{14}H_4N_6O_{10}$: C, 40.39; H, 0.97; N, 20.19. Found: C, 40.73; H, 1.00; N, 20.31.

2,2',6,6'-Tetranitrobiphenyl-4,4'-dicarboxhydrazide (III).

Five g. (0.0011 mole) of 4,4'-dicarbomethoxy-2,2',6,6'-tetranitrobiphenyl (IIc) was dissolved in 800 ml. of boiling absolute ethanol. To this solution 7.0 ml. of 42% hydrazine hydrate was added dropwise. The solution was allowed to reflux for 18 hours and the volume was reduced to ~400 ml. The dark solution was treated with charcoal and concentrated further. On cooling buff colored crystals (III) were obtained, 1.6 g. (32%). The analytical sample was recrystallized from ethanol, buff colored crystals, m.p. 267-269° dec.; U.V. λ max (95% ethanol), 208 (ϵ , 48,660), 228 (ϵ , 45,450), 239 μ (ϵ , 45,740).

Anal. Calcd. for $C_{14}H_{10}N_8O_{10}$: C, 37.35; H, 2.24; N, 24.88. Found: C, 37.49; H, 2.31; N, 24.63.

4,4'-Diacetamido-2,2',6,6'-tetranitrobiphenyl (IIj).

To 75 ml. of acetic anhydride, 5.19 g. (0.0011 mole) of 2,2',6,6'-tetranitrobiphenyl-4,4'-dicarboxazide (IIg) and 5 drops of concentrated sulfuric acid were added and the mixture was heated slowly with stirring in an oil bath. The temperature of the oil bath was increased to 135° and kept at this temperature for 3.5 hours until nitrogen evolution had ceased. The clear solution was cooled to room temperature and added with stirring to 600 ml. of water. The gummy residue, which separated in water gave a brown powder on stirring overnight with a magnetic stirrer. The brown powder was filtered, washed with water and dried to give 4.7 g. (98% crude) of product. In some instances at this stage the triacetamide was isolated, m.p. 183°, which on boiling with aqueous ethanol hydrolyzed to IIj. The crude product was purified on a neutral alumina (Woelm grade III) column using ethyl acetate as the eluent. A yellow product was obtained which when recrystallized from aqueous ethanol gave yellow needles, m.p. 325° dec.; U.V. λ max (95% ethanol), 246 (ϵ , 69,950), 295(sh) (ϵ , 16,720), 342 μ (ϵ , 5,490); NMR (deuterioacetone, external standard) δ 9.65 (broad peak-2H, NH), δ 8.25 (singlet-4H, aromatic), δ 1.66 (singlet-6H, methyl).

Anal. Calcd. for $C_{16}H_{12}N_6O_{10}$: C, 42.86; H, 2.67; N, 18.75. Found: C, 43.16; H, 2.59; N, 18.86.

4,4'-Diamino-2,2',6,6'-tetranitrobiphenyl (IIk).

Method A.

2,2',6,6'-Tetranitrobiphenyl-4,4'-dicarboxamide (IIf) (2.7 g. 0.0065 mole) was added all at once to a cold solution of sodium hypobromite at 0°, prepared by dissolving 2.6 g. of sodium hydroxide in 25 ml. of water and adding 1 ml. of bromine at 0°. The reaction mixture was stirred at 0° for 10 minutes and then heated to boiling for 5 minutes. The reaction mixture was cooled, filtered and washed with water to give a brown residue (1.1 g.). The aqueous solution was saturated with sodium chloride and extracted in a continuous ether extractor for 24 hours to give an additional 0.3 g. of the product. The brown residue was purified on a neutral alumina (Woelm grade III) column, 15 g., using ethyl acetate as eluent. The first yellow fraction gave pure IIk, yield (10-40%). The analytical sample was obtained by recrystallization from ether-petroleum ether, yellow microcrystals, m.p. 300° dec., mildly explodes at ~365° on rapid heating; U.V. λ max (95% ethanol), 238 (ϵ , 91,440), 305(sh) μ ; NMR (deuterioacetone, external standard) δ 7.13 (singlet-4H, aromatic), δ 5.62 (broad peak-4H, NH₂).

Anal. Calcd. for $C_{12}H_8N_6O_8$: C, 39.58; H, 2.21; N, 23.09. Found: C, 39.47; H, 2.40; N, 22.91.

Method B.

Crude 4,4'-diacetamido-2,2',6,6'-tetranitrobiphenyl (IIj) (4.9 g., 0.0011 mole) was added to 30 ml. of 50% sulfuric acid. The mixture was refluxed for 4 hours, cooled to room temperature and diluted with 100 ml. of water to give a yellow precipitate. The aqueous mixture was extracted with 3 x 75 ml. of ethyl acetate. The combined ethyl acetate extracts were washed once with 25 ml. of water and dried over anhydrous magnesium sulfate. The ethyl acetate extract was evaporated to dryness to give 3.7 g. (92%) of the yellow product which was purified on a neutral alumina column and recrystallized as in Method A to give the identical product. 4,4'-Dichloro-2,2',6,6'-tetranitrobiphenyl (IIIm).

To 7.5 ml. of 66% sulfuric acid at 0°, 0.5 g. of 4,4'-diamino-2,2',6,6'-tetranitrobiphenyl (IIk) was added while stirring. To this suspension, 1 ml. of cold 50% sodium nitrate solution was added at the bottom of the mixture while stirring. Stirring was continued at 0° for 10 minutes whereupon a white precipitate formed and was allowed to stand for 10 minutes at 0°. This mixture was added portionwise to 0.5 g. of cuprous chloride dissolved in 5 ml. of concentrated hydrochloric acid. At this stage the mixture frothed. After dilution with water it was extracted with 2 x 25 ml. of chloroform. The chloroform extract was dried over anhydrous magnesium sulfate and evaporated to dryness giving a yellow powder. Recrystallization from ligroin (60-80°) gave pale yellow crystals m.p. 210°; U.V. λ max (95% ethanol), 207 (ϵ , 61,230), 240 μ (ϵ , 36,220); NMR (deuteriochloroform) δ 8.36 (singlet).

Anal. Calcd. for $C_{12}H_4Cl_2N_4O_8$: C, 35.75; H, 1.00; N, 13.90. Found: C, 36.11; H, 1.17; N, 14.13.

2,9-Dimethyl-1,10-dinitrobenzo[c]cinnoline (VII).

Three g. (0.0144 mole) of 2,9-dimethylbenzo[c]cinnoline was added portionwise to a mixture of 20 ml. of concentrated sulfuric acid and 20 ml. of red fuming nitric acid at 0-5°. The mixture was stirred at 20° for 45 minutes and poured on ice. The precipitate was collected by filtration washed with water and dried. The compound was purified on a neutral alumina (Woelm grade III) column using chloroform as the eluent. The chloroform was evaporated to dryness and the residue was dissolved in ether, the solution was filtered and dried to give 3.7 g. (51%) of the product, yellow crystals, m.p. 220° (darkens) and melts at 255°, dec.; U.V. λ max (95% ethanol), 232 (ϵ , 44,560), 284 (ϵ , 21,800), 319 (sh) μ (ϵ , 9,930); NMR (deuteriochloroform), δ 8.96 (doublet, $J = 8.5$ cps, 3 and 8 protons), δ 8.04 (doublet, $J = 8.5$ cps, 4 and 7 protons), δ 2.81 (singlet-6H, two methyl groups).

Anal. Calcd. for $C_{14}H_{10}N_4O_4$: C, 56.38; H, 3.40; N, 18.80. Found: C, 56.64; H, 3.38; N, 18.78.

2,7-Dimethyl-4,5,9,10-tetraazapyrene Di-N-oxide (IIIa).

Method A.

Two g. (0.0055 mole) of 4,4'-dimethyl-2,2',6,6'-tetranitrobiphenyl (IIa) was added to 500 ml. of absolute ethanol containing 1 ml. of 4% sodium hydroxide. To this W-7 Raney-nickel catalyst (aged 10 weeks) was added and the mixture was hydrogenated at atmospheric pressure and room temperature until about two-thirds of the theoretical amount of hydrogen had been absorbed whereupon formation of a dark yellow precipitate took place. The mixture was filtered and the residue was extracted with boiling nitrobenzene. The nitrobenzene solution was concentrated and cooled to give 0.60 g. (49%) of yellow crystals. After recrystallization from nitrobenzene the product had m.p. > 300° dec.; U.V. λ max (95% ethanol), 228 (ϵ , 46,950), 250 (sh) (ϵ , 28,510), 267 (ϵ , 20,970), 277 (ϵ , 21,170), 289 (sh) (ϵ , 18,990), 310 (ϵ , 8,440), 324 (ϵ , 8,166), 368 (ϵ , 8,700), 411 (ϵ , 9,350), 435 μ (ϵ , 9,675); infrared cm^{-1} : 3450(b), 3090(w), 1675(w), 1555(s), 1470(s), 1450(s), 1400(m), 1330(w), 1240(w), 1195(m), 1145(w), 865(m), 815(m), 800(w), 735(w), 722(m), 610(w), 540(m).

Anal. Calcd. for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 63.39; H, 3.71; N, 20.76.

Method B.

One tenth g. of 2,7-dimethyl-4,5,9,10-tetraazapyrene (VI) in 100 ml. of acetic acid was treated with 4 ml. of 50% hydrogen peroxide at room temperature and the mixture was allowed to stir overnight. Then 2 ml. of 50% hydrogen peroxide was added and

stirring was continued for an additional 20 hours. To this 100 ml. of water was added and the mixture allowed to stand overnight. The product was collected by filtration, dried and recrystallized from nitrobenzene giving 75 mg. (63%) of IIIa, yellow crystals, m.p. > 300° dec. Ultraviolet and infrared spectra are identical to the spectra obtained with the compound prepared by Method A.

2,7-Dimethoxy-4,5,9,10-tetraazapyrene Di-N-oxide (IIIb).

This compound was prepared in 40-50% yield by a procedure similar to that for IIIa (Method A). After recrystallization from nitrobenzene, orange needles, m.p. > 300° dec. were obtained; U.V. λ max (95% ethanol-saturated solution), 257 (sh), 280, 370 μ ; infrared cm^{-1} : 3450(b), 3100(m), 1680(m), 1555(s), 1520(m), 1480(s), 1460(s), 1445(m), 1420(s), 1350(w), 1330(s), 1275(w), 1222(m), 1185(m), 1172(s), 1145(m), 1100(w), 1070(s), 1005(w), 988(w), 970(m), 910(w), 880(w), 868(w), 815(m), 805(m), 765(w), 720(w), 610(w), 575(w), 540(w).

Anal. Calcd. for $C_{14}H_{10}N_4O_4$: C, 56.38; H, 3.38; N, 18.78. Found: C, 56.65; H, 3.40; N, 18.54.

2,7-Diacetamido-4,5,9,10-tetraazapyrene Di-N-oxide (IIIc).

4,4'-Diacetamido-2,2',6,6'-tetranitrobiphenyl (IIj) (1.12 g., 0.0025 mole) was dissolved in 100 ml. of absolute ethanol containing 0.5 ml. of 4% sodium hydroxide solution. To this reddish solution W-7 Raney-nickel catalyst (aged 10 weeks) was added and the mixture was hydrogenated for 6 hours at atmospheric pressure and room temperature during which time 400 ml. of hydrogen was absorbed. The clear solution became gelatinous during hydrogenation so more ethanol was added and the solution was filtered under vacuum. The residue was washed with alcohol, dried and extracted with ~100 ml. of hot dimethylformamide. The dimethylformamide solution was cooled and diluted with ether and on cooling a yellow powder (0.3 g.) precipitated. It was filtered and recrystallized twice from dimethylformamide, brownish-yellow crystals, 0.2 g. (23%) IIIc, m.p. > 300° dec.; U.V. λ max (95% ethanol-saturated solution) 228 (sh), 278, 305 (sh), 360 μ ; infrared cm^{-1} : 3450(b), 3350(b), 3150(w), 3075(w), 1670(s), 1580(s), 1530(s), 1470(s), 1398(m), 1370(s), 1330(w), 1270(s), 1200(w), 1168(m), 1145(w), 1090(w), 1045(m), 1010(w), 993(w), 870(m), 840(w), 720(w).

Anal. Calcd. for $C_{16}H_{12}N_6O_4$: C, 54.55; H, 3.43; N, 23.86. Found: C, 54.72; H, 3.47; N, 23.95.

4,4'-Dicarbomethoxy-2,2',6,6'-tetraaminobiphenyl (IV).

To 500 ml. of absolute ethanol 8.1 g. (0.018 mole) of 4,4'-diacetamido-2,2',6,6'-tetranitrobiphenyl (IIj) and W-2 Raney-nickel catalyst was added and the mixture was hydrogenated at room temperature and at atmospheric pressure until 8 liters of hydrogen had been absorbed. The mixture was filtered and the filtrate was evaporated to dryness to give 5 g. of green powder. This was dissolved in ethanol-benzene, treated with charcoal and after evaporation was recrystallized from benzene-hexane to give white crystals, 3.5 g. (59%) of IV, m.p. 223-225°; U.V. λ max (95% ethanol), 222 (ϵ , 56,400), 241 (ϵ , 38,720), 281 (ϵ , 15,160), 338 μ (ϵ , 7,340).

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 57.93; H, 5.31; N, 16.67.

2,7-Dicarbomethoxy-4,5,9,10-tetraazapyrene (V).

4,4'-Dicarbomethoxy-2,2',6,6'-tetraaminobiphenyl (IV) (3.2 g., 0.0097 mole) was added to 400 ml. of dry benzene containing 12.9 g. of phenyliodosoacetate and the mixture was allowed to stir at room temperature. After 1 hour the mixture became dark brown and stirring was continued for 20 hours. The mixture

was filtered, and the residue was dried and dissolved in hot dimethylformamide. On cooling the dimethylformamide solution a brownish-red crystalline solid separated. Recrystallization from dimethylformamide gave 0.55 g. (18%) of V, m.p. 275-280° dec.; U.V. λ max (95% ethanol) 262 (ϵ , 50,680), 284 (sh) (ϵ , 20,860), 323 (sh) (ϵ , 8,690), 334 (ϵ , 11,501), 344 (ϵ , 11,580), 376 (ϵ , 1,754), 395 $m\mu$ (ϵ , 1,400); infrared cm^{-1} : 3400(b), 3050(m), 2950(w), 1730(vs), 1625(w), 1545(w), 1445(w), 1425(m), 1380(m), 1355(w), 1330(s), 1295(w), 1258(vs), 1248(sh), 1142(m), 1100(w), 1020(m), 992(m), 972(w), 925(m), 905(w), 770(s), 758(m).

Anal. Calcd. for $C_{16}H_{10}N_4O_4$: C, 59.63; H, 3.13; N, 17.39. Found: C, 59.74; H, 3.14; N, 17.34.

2,7-Dimethyl-4,5,9,10-tetraazapyrene (VI)

4,4'-Dimethyl-2,2',6,6'-tetranitrobiphenyl (IIa) (1.7 g., 0.0047 mole) was added to 300 ml. of absolute ethanol containing 2 ml. of 10% sodium hydroxide solution and freshly prepared W-2 Raney-nickel catalyst. The mixture was hydrogenated at atmospheric pressure and at room temperature for 4 hours whereupon 940 ml. of hydrogen was adsorbed. The mixture was filtered and the residue was extracted with 2 x 100 ml. of hot dimethylformamide. After cooling 0.225 g. (20%) of VI as feathery brown needles separated. Recrystallization from dimethylformamide gave a product, m.p. > 300° dec.; U.V. λ max (95% ethanol), 224 (ϵ , 62,300), 243 (ϵ , 71,370), 255 (sh) (ϵ , 30,790), 263 (ϵ , 27,550), 342 (ϵ , 23,740), 353 (ϵ , 21,580), 391 (ϵ , 6,620), 411 $m\mu$ (ϵ , 11,510); infrared cm^{-1} : 3045(s), 1850(w), 1605(m), 1555(m), 1470(m), 1390(m), 1305(s), 1238(s), 1228(s), 1148(s), 1137(m), 1040(w), 1015(s), 958(s), 921(m), 862(s), 853(s), 712(m), 552(s), 530(m).

Anal. Calcd. for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.82; H, 4.30; N, 23.77.

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