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RESEARCH ON PHENANTHRIDONE AND TETRAHYDRODIAZAPYRENE.

2.\* SYNTHESIS OF 2,7-DIAMINO-5,10-DIOXO-4,5,9,10-

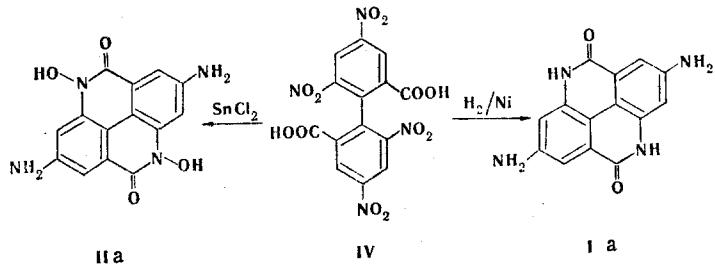
TETRAHYDRO-4,9-DIAZAPYRENE AND ITS DERIVATIVES

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The synthesis of 2,7-diamino-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyprene (Ia) and its 4,9-dihydroxy derivative (IIa) from diphenic acid (III) is described. 4,4',6,6'-Tetranitrodiphenic acid (IV) was obtained by nitration of III. Reduction of IV with iron or with hydrogen over Raney nickel gave Ia, while reduction with stannous chloride gave IIa. Diacetyl and tetraacetyl derivatives of Ia and IIa were obtained. The amino groups in Ia and IIa were replaced by H, Cl, Br, I, CN, NO<sub>2</sub>, and OH through diazotization. It is shown that II and its derivatives can be reduced with iron or with hydrogen over a nickel catalyst to compounds of the 5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyprene series.

The synthesis of 2,7-diamino-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyprene (Ia) and its 4,9-dihydroxy derivative (IIa) from diphenic acid (III) is proposed in the present paper. Treatment of acid III with a nitrating mixture gave 4,4',6,6'-tetranitrodiphenic acid (IV) in up to 90% yield; acid IV was previously obtained by the Ullmann reaction [1] or through nitro-substituted phenanthrenequinones [2]. The reduction of tetranitro compound IV with stannous chloride was described in [3]. The Ia structure was erroneously assigned to the reaction product. In a preliminary communication [4] we demonstrated that the structure of the product of the reduction of IV with stannous chloride is described by structural formula IIa.

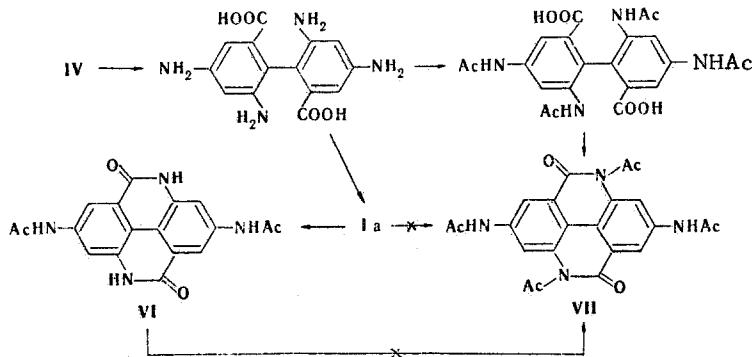


When diamine IIa is heated with acetic anhydride, it undergoes both N acylation and O acylation to give 2,7-diacetamido-4,9-diacetoxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyprene (V). A solution of diamine IIa in dimethylformamide (DMF) takes on the intensely red coloration that is characteristic for N(OH) groups in the ortho position relative to a carbonyl group [5] when trivalent iron salts are added. The deamination of diamine IIa through diazotization and subsequent reduction gives IIb, the IR spectrum of which is identical to the spectrum of the compound obtained by the reduction of 6,6'-dinitrodiphenic acid with zinc in a neutral medium [6]. Compound IIa cannot be reduced further even with excess stannous chloride.

\*See [4] for communication 1.

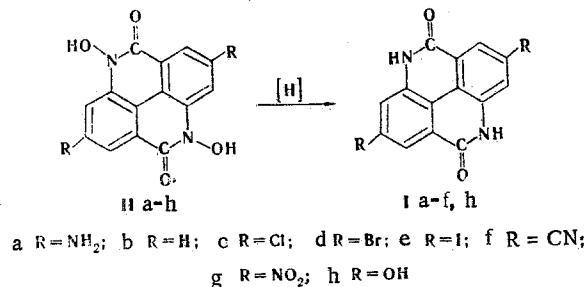
Scientific-Research Institute of Plastics, Moscow 111112. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1672-1677, December, 1979. Original article submitted August 31, 1978; revision submitted June 27, 1979.

We obtained the product of more nearly complete reduction of tetrinitro acid IV, viz., diamine Ia, by reduction with hydrogen over Raney nickel or with iron in an electrolyte medium. A solution of Ia does not form colored complexes with iron ions. The deamination of Ia gave Ib, the IR spectrum of which is identical to the spectrum of the compound previously obtained by oxidation of 4,9-diazapyrene [7]. 2,7-Diacetyl derivative VI was obtained by acetylation of diamine Ia with acetic anhydride. The tetraacetyl derivative of diamine Ia was obtained by reduction of IV with iron in acetic anhydride. This makes it possible to propose the following pathway for the formation of tetraacetyl derivative VII:



Compound IV is not reduced by iron powder in formic acid.

The anomalous result obtained in the reduction of IV with stannous chloride can be explained by the inhibiting effect of the intramolecular hydrogen bonds on the reduction of the nitro and hydroxamic acid groups. We have previously [8-10] observed the existence of such bonds between the  $\text{NO}_2$  and  $\text{COOH}$  groups in nitro acid IV and between the CO and  $\text{N}(\text{OH})$  groups in compounds of the IIa type, and their effect on reduction has been noted repeatedly [11]. The presence of tin ions additionally stabilizes the reaction center at the hydroxamic acid groups, since it leads to the formation of an insoluble complex, which precipitates. Additional treatment of IIa with stannous chloride or an excess of the latter in the reduction of acid IV therefore does not lead to further reduction to diamine Ia. Compounds with a hydroxamic acid group (IIa-h) can be reduced to lactams (Ia-f, h) when one uses iron powder in an electrolyte medium or hydrogen over Raney nickel as the reducing agent. Diamine Ia was obtained in the reduction of IIg ( $\text{R} = \text{NO}_2$ ) under the same conditions.



The data from the IR spectra of crystalline Ia-i and IIa-h show that the CO, NH,  $\text{N}(\text{OH})$ ,  $\text{NH}_2$ , and OH groups are associated. Strong intermolecular hydrogen bonds constitute the reason for the high melting points of these compounds and their low solubilities in organic solvents. Analytical samples of these substances were obtained by sublimation at 300-360°C and a residual pressure of up to  $10^{-3}$  mm,\* as well as by recrystallization from DMF and dimethyl sulfoxide (DMSO). Many of them fluoresce when they are irradiated with UV light.

Diamines Ia and IIa are diazotized under normal conditions. The diazo groups are replaced by hydroxy groups when suspensions of the diazo compounds are heated in dilute sulfuric acid. The diazo groups are also readily replaced by chlorine, bromine, and iodine and by the cyano group. Treatment of diamine Ia with phosgene in nitrobenzene leads to a di-isocyanato derivative (Ii). The diazo compounds from diamines Ia and IIa readily undergo diazo coupling with azo components to give disazo dyes that contain 4,9-dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene and 5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene rings and have increased direct dyeing character.

## EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrophotometer. The purity of the synthesized compounds was monitored on Silufol UV-254 plates. The analytical data and the IR spectra of Ia-k and IIa-h are presented in Tables 1 and 2.

4,4',6,6'-Tetranitrodiphenic Acid (IV). A 60.6-g (0.25 mole) sample of diphenic acid was added to a mixture of 80 ml (1.9 moles) of nitric acid (sp. gr. 1.51) and 400 ml of sulfuric acid, and the resulting mixture was stirred at 50°C for 20 min. The temperature was then raised to 100°C, and the mixture was heated at this temperature for 1 h. It was then cooled and poured over 2.5 kg of ice, and the white precipitate was removed by filtration, washed with water, and dried to give 95 g (90%) of a product with mp 293°C (from water) [mp 293-293.5°C (dec.) [2]].

2,7-Diamino-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (Ia). A 75-g (1.34 g-atoms) sample of iron powder was added to 175 ml of 5% aqueous ammonium chloride solution, the mixture was heated with vigorous stirring on a boiling-water bath, and a solution of 42 g (0.1 mole) of nitro acid IV in 150 ml of 10% ammonium hydroxide was added in the course of 1 h. The mixture was then stirred for 30 min, 45 ml of 20% alkali solution was added, and the resulting precipitate was removed by filtration and treated several times with a boiling mixture (2:1) of DMF and 25% sodium hydroxide solution. The filtrates were combined and acidified to pH 5 with hydrochloric acid, and the yellow precipitate was removed by filtration to give 24 g (88%) of product. An analytical sample was obtained by sublimation at 360°C (10<sup>-3</sup> mm) and had mp > 400°C and R<sub>f</sub> 0.5 [25% ammonium hydroxide-dioxane (1:5)]; the compound had green luminescence when it was irradiated with UV light.

B) A 42-g (0.1 mole) sample of IV was added to 470 ml of dioxane in a 1-liter autoclave, 8 g of Raney nickel was added, and a hydrogen pressure of 85 atm was created. The mixture was then heated to 95°C in the course of an hour and stirred vigorously for 6 h. The suspension in dioxane was separated from the catalyst to give 23 g (84%) of diamine Ia.

C) A 3-g (0.01 mole) sample of diamine IIa was reduced under the conditions of experiment A to give 2.2 g (81%) of Ia.

D) A 1.8-g (5 mmole) sample of dinitro compound IIg was reduced under the conditions of experiment A to give 1 g (74%) of Ia.

The sulfate of Ia was obtained as greenish crystals with mp > 400°C. Found: C 45.9, H 3.4; N 15.3; S 8.6%. C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub>. Calculated: C 46.1; H 3.3; N 15.4; S 8.8%.

2,7-Diacetamido-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VI). A 2.7-g (0.01 mole) sample of Ia was refluxed for 30 min in 50 ml of acetic anhydride, and the gray pre-

TABLE 1. 2,7-Disubstituted 5,10-Dioxo-4,5,9,10-tetrahydro-4,9-diazapyrenes (Ia-i)

Compound	R	IR spectrum, cm <sup>-1</sup> (in KBr)	Found, %			Empirical formula*	Calc., %			Yield, %
			C	H	N		C	H	N	
Ia	NH <sub>2</sub>	3430-3350 (NH <sub>2</sub> ), 2940 (NH), 1660 (C=O)	63.1	3.8	21.0	C <sub>14</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	63.2	3.8	21.1	88
Ib	H	3100-2900 (NH), 1660 (C=O)	70.9	3.6	11.8	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	71.2	3.4	11.9	85
Ic	Cl	3220-2900 (NH), 1670 (C=O)	55.1	2.1	9.2	C <sub>14</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	55.1	2.0	9.0	93
Id	Br	3175-2900 (NH), 1665 (C=O)	42.6	1.5	7.1	C <sub>14</sub> H <sub>6</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	42.7	1.5	7.1	88
Ie	I	3170-2900 (NH), 1660 (C=O)	34.1	1.5	5.6	C <sub>14</sub> H <sub>6</sub> I <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	34.4	1.3	5.7	81
If	CN	2990 (NH), 1665 (C=O)	67.0	2.2	19.7	C <sub>16</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>	67.2	2.1	19.6	82
Ig	NO <sub>2</sub>	3070 (NH), 1680 (C=O), 1535 (NO <sub>2</sub> ), 1350 (NO <sub>2</sub> )	51.4	1.8	17.1	C <sub>14</sub> H <sub>6</sub> N <sub>4</sub> O <sub>6</sub>	51.5	1.8	17.2	80
Ih	OH	3300-2900 (NH, OH), 1670 (C=O)	62.6	3.1	10.7	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>	62.7	3.0	10.5	84
Ii	NCO	3200-2900 (NH), 2280 (NCO), 1670 (C=O)	60.2	1.8	17.4	C <sub>16</sub> H <sub>6</sub> N <sub>4</sub> O <sub>4</sub>	61.4	3.4	7.9	85

\*The compositions of Ic-e were also confirmed by determination of the halogen content.

TABLE 2. 2,7-Disubstituted 4,9-Dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrenes (IIa-h)

Com- ound	R	IR spectrum (in KBR), cm <sup>-1</sup>	Found, %			Empirical formula*	Calc., %			Yield
			C	H	N		C	H	N	
IIa	NH <sub>2</sub>	3345 (NH <sub>2</sub> ), 3100 (OH), 1650 (C=O)	56.3	3.5	18.7	C <sub>14</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub>	56.4	3.4	18.8	61
IIb	H	3200-3100 (OH), 1660 (C=O)	63.1	3.2	10.4	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>	62.7	3.0	10.4	90
IIc	Cl	3100 (OH), 1670 (C=O)	49.8	1.9	8.1	C <sub>14</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	49.9	1.8	8.3	89
IId	Br	3100 (OH), 1665 (C=O)	39.5	1.3	6.5	C <sub>14</sub> H <sub>6</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	39.5	1.3	6.6	91
IIe	I	3100 (OH), 1660 (C=O)	32.3	1.2	5.4	C <sub>14</sub> H <sub>6</sub> I <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	32.3	1.2	5.4	92
IIf	CN	3100 (OH), 1665 (C=O)	60.3	2.0	17.7	C <sub>16</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>	60.4	1.9	17.6	91
IIg	NO <sub>2</sub>	3100 (OH), 1670 (C=O), 1535 (NO <sub>2</sub> ), 1350 (NO <sub>2</sub> )	47.0	1.6	15.7	C <sub>14</sub> H <sub>6</sub> N <sub>2</sub> O <sub>8</sub>	46.9	1.7	15.6	87
IIh	OH	3200-3100 (OH), 1670 (C=O)	55.9	2.4	9.5	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> O <sub>6</sub>	56.0	2.7	9.3	84

\*The compositions of IIc-e were also confirmed by determination of the halogen content.

cipitate was removed by filtration and washed with acetic acid and water to give 3.2 g (91%) of VI with mp >400°C (from DMF). IR spectrum: 3000 (NH), 1690 (acetyl C=O), and 1660 cm<sup>-1</sup> (lactam C=O). Found: C 61.3; H 4.2; N 15.7%. C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>. Calculated: C 61.7; H 4.0; N 16.0%.

2,7-Diacetamido-4,9-diacetyl-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VII). A 7.8-g (0.14 g-atom) sample of iron powder was stirred in 40 ml of acetic anhydride, the mixture was heated to 100°C, and 4.2 g (0.01 mole) of nitro acid IV was added. The mixture was stirred for 1 h, and the product was isolated from the sediment by extraction with boiling DMF to give 3.5 g (80%) of VII with mp > 400°C (yellow crystals from DMF). IR spectrum: 1690 (acetyl C=O) and 1670 cm<sup>-1</sup> (lactam C=O). Found: C 60.3; H 4.2; N 13.0%. C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>O<sub>6</sub>. Calculated: C 60.8; H 4.1; N 12.9%.

2,7-Diamino-4,9-dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (IIa). Hydrochloric acid (150 ml) was added to a solution of 42 g (0.1 mole) of acid IV in 400 ml of acetic acid, the mixture was heated on a boiling-water bath, and a solution of 350 g (1.5 mole) of stannous chloride in 300 ml of concentrated hydrochloric acid was added with stirring in the course of 40 min. The mixture was then heated on a boiling-water bath for another hour. As the reduction proceeded, the solution turned red, and a yellow precipitate subsequently formed. The precipitate was removed by filtration and dissolved in concentrated sulfuric acid, and the acid solution was poured over ice. The precipitate was removed by filtration, washed with water, and dried to give 24.3 g of sulfate IIa. The sulfate was converted to base IIa by heating in 10% alkali solution.

An analytical sample was obtained by sublimation at 340°C (10<sup>-3</sup> mm). The yellow crystals had mp > 400°C and R<sub>f</sub> 0.84 [25% ammonium hydroxide-dioxane (4:5)]; the product had greenish-blue luminescence in UV light.

Hydrochloride of IIa. This compound was obtained as yellowish crystals with mp > 400°C. Found: C 45.5; H 3.2; Cl 18.9; N 14.9%. C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>·2HCl. Calculated: C 45.3; H 3.3; Cl 19.1; N 15.1%.

Sulfate of IIa. This compound was obtained as greenish-yellow crystals with mp > 400°C. Found: C 42.2; H 3.1; N 14.2; S 8.0%. C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>·H<sub>2</sub>SO<sub>4</sub>. Calculated: C 42.4; H 3.0; N 14.1; S 8.1%.

2,7-Diacetamido-4,9-diacetoxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (V). A 3-g (0.01 mole) sample of diamine IIa was refluxed for 40 min in 50 ml of acetic anhydride, and the grayish precipitate was removed by filtration and washed with acetic acid and water to give 4.2 g (90%) of V with mp > 400°C (from DMF). Found: C 56.7; H 3.9; N 12.1%. C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>O<sub>8</sub>. Calculated: C 56.7; H 3.9; N 12.0%.

4,9-Dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (IIb). A 3-g (0.01 mole) sample of diamine IIa was dissolved in 30 ml of concentrated sulfuric acid, and the solution was poured into 70 ml of water. The resulting suspension was cooled to 5°C, and 4.6 ml (0.02 mole) of a 30% solution of sodium nitrite was added gradually. A solution of 60 g (0.57 mole) of sodium hypophosphite in 60 ml of 25% hydrochloric acid and 0.02 g (0.08 mmole)

of copper sulfate were added to the suspension of the bisdiazoo compound, and the precipitate was removed by filtration after 24 h to give 2.52 g (90%) of IIb. An analytical sample was obtained by sublimation at 300°C (0.5 mm) and had mp > 400°C and R<sub>f</sub> 0.34 [25% ammonium hydroxide-dioxane (3:5)]; the product had greenish-yellow fluorescence in UV light.

Compound Ib, with mp > 400°C and R<sub>f</sub> 0.48 [25% ammonium hydroxide-dioxane (1:3)], was similarly obtained from diamine Ia.

4,9-Diacetoxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene. A 1.35-g (5 mmole) sample of IIb was refluxed in 50 ml of acetic anhydride, after which the mixture was cooled and poured into 100 ml of water to give 1.6 g (91%) of a product with mp > 400°C (from DMF). IR spectrum: 1690 (acetyl C=O) and 1665 cm<sup>-1</sup> (lactam C=O). Found: C 61.3; H 3.4; N 7.9%. C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>. Calculated: C 61.5; H 3.4; N 8.0%.

2,7-Dichloro-4,9-dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (IIc). A 1.5-g (5 mmole) sample of diamine IIa was heated at 80°C in 30 ml of 15% hydrochloric acid for 10 min, after which the mixture was cooled to 5°C and diazotized with 2.3 ml (10 mmole) of a 30% solution of sodium nitrite with stirring for 1 h. A 3-g (15.1 mmole) sample of Cu<sub>2</sub>Cl<sub>2</sub> was added to the suspension of the bisdiazoo compound, and the mixture was stirred for 1 h and allowed to stand overnight. The mixture was then heated to 100°C, maintained at this temperature for 1 h, and cooled, and the precipitate was removed by filtration to give 1.51 g of IIc with mp > 400°C (yellowish crystals from DMSO). Compound Ic was similarly obtained.

2,7-Dibromo-4,9-dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (IId). A 1.5-g (5 mmole) sample of diamine IIa was added to 30 ml of 48% HBr solution, the mixture was cooled with stirring to 0°C, 2.3 ml (10 mmole) of 30% sodium nitrite solution was added, and the mixture was stirred for 1 h. A 30-g (37.8 mmole) sample of 15% potassium bromide solution, 1 g (6.2 mmole) of bromine, and 0.1 g (0.42 mmole) of crystalline copper sulfate were added, and the mixture was stirred for 12 h. The light-brown precipitate was removed by filtration to give 1.94 g of IId with mp > 400°C (from DMF).

Compound Id was similarly obtained.

2,7-Diiodo-4,9-dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (IIe). A 3-g (10 mmole) sample of diamine IIa was dissolved in 15 ml (0.26 mole) of concentrated sulfuric acid, and the mixture was poured over 50 g of ice. The resulting suspension was diazotized by adding 4.6 ml (20 mmole) of 30% sodium nitrite solution and stirring at 0-5°C for 50 min. A 30-g (54.2 mmole) sample of 30% potassium iodide solution and 0.51 g (2 mmole) of iodine were added to the bisdiazoo compound, and the mixture was stirred at 5°C for 1 h and allowed to stand for 12 h. The grayish product was removed by filtration to give 4.8 g of IIe. An analytical sample was obtained by recrystallization from DMF. The yellow crystals had mp > 400°C.

Compound Ie was similarly obtained.

2,7-Dicyano-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (If). A 2.7-g (10 mmole) sample of diamine Ia was diazotized under the conditions for the preparation of IIb, and the resulting bisdiazoo compound was stirred at 5°C for 2 h. A 5.2 g (21.7 mmole) sample of crystalline copper sulfate and 5.8 g (85.7 mmole) of 96% potassium cyanide in 40 ml of water were added to the heated (to 90°C) solution, and the mixture was stirred at 95-100°C for 1 h. Workup gave 2.35 g of If with mp > 400°C (from DMF).

Compound IIIf was similarly obtained.

2,7-Dinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (Ig). A 1.33-g (5 mmole) sample of diamine Ia was dissolved in 10 ml (0.17 mole) of concentrated sulfuric acid, and the solution was poured over 30 g of ice. A 2.3-ml (10 mmole) sample of 30% sodium nitrite solution was added at 5°C, the mixture was stirred for 1 h, and the resulting suspension of the bisdiazoo compound was added in portions at 60°C to a stirred solution of 18 g (0.26 mole) of sodium nitrate and 10 g (0.12 mole) of sodium bicarbonate in 150 ml of water. The mixture was stirred for 30 min, after which the precipitate was removed by filtration and washed to give 1.3 g of Ig. Recrystallization from DMF-water (2:1) gave yellowish needles with mp > 400°C and R<sub>f</sub> 0.83 [ammonia-dioxane (1:4)].

Compound IIg was similarly obtained.

2,4,7,9-Tetrahydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (IIh). A 3.0-g (10 mmole) sample of diamine IIa was diazotized in sulfuric acid under the conditions for

the preparation of IIb, and 0.1 g (0.4 mmole) of crystalline copper sulfate was added to the suspension of the bisdiazo compound. The mixture was heated gradually to 100°C and maintained at this temperature for 2 h, after which it was cooled, and the precipitate was removed by filtration to give 2.52 g of IIh with mp > 400°C (DMF) and R<sub>f</sub> 0.18 [ammonia-dioxane (1:3)]; the product had blue luminescence in UV light.

Compound Ih, with mp > 400°C (from DMF) and R<sub>f</sub> 0.81 [25% ammonium hydroxide-dioxane (1:4)], was similarly obtained; the product had blue fluorescence in UV light.

2,4,7,9-Tetraacetoxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene. A 3.0-g (10 mmole) sample of IIh was added to 50 ml of DMF, 10 g (98.1 mmole) of acetic anhydride was added, and the mixture was refluxed for 30 min. It was then cooled and poured into 100 ml of water, and the aqueous mixture was worked up to give 4.26 g (91%) of a product with mp > 400°C [DMF-water (2:1)]. IR spectrum: 3080 (NH), 1690 (acetyl C=O), and 1665 cm<sup>-1</sup> (lactam C=O). Found: C 56.6; H 3.4; N 5.9%. C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>10</sub>. Calculated: C 56.4; H 3.4; N 6.0%.

Similarly, 2,7-diacetoxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene, with mp > 400°C, was obtained from Ih. IR spectrum: 3080 (NH), 1690 (acetyl C=O), and 1665 cm<sup>-1</sup> (lactam C=O). Found: C 61.3; H 3.4; N 7.9%. C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>. Calculated: C 61.4; H 3.4; N 7.9%.

2,7-Diisocyanato-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (Ii). A previously dried and distilled 65-ml sample of nitrobenzene was cooled to 7°C, 3.5 g (0.035 mole) of liquid phosgene was added, and a suspension of 13.3 g (0.05 mole) of diamine Ia in 50 ml of nitrobenzene was added in portions with stirring. The mixture was then stirred at 7°C for 1 h, after which it was heated to 180°C for 1.5 h, and phosgene gas was bubbled through the mixture at this temperature for 2 h. Workup gave 13.5 g of diisocyanato derivative Ii with mp > 320°C (dec.).

Reduction of IIa-h (General Method). A 7-g (0.125 g-atom) sample of iron powder and 0.2 g of ammonium chloride were stirred in 40 ml of 50% aqueous DMF at 100°C, 0.01 mole of IIa-h was added, and the mixture was stirred for 1 h. The product was extracted from the sediment with boiling DMF. This procedure gave Ia-f, h in 80-85% yields.

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