# INVESTIGATION OF PHENANTHRIDONE AND DIOXOTETRAHYDRODIAZAPYRENE.

# 4.* SYNTHESIS OF AMINO-SUBSTITUTED PHENANTHRIDONES AND DIOXOTETRAHYDRODIAZAPYRENES

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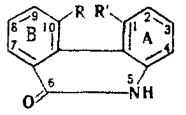
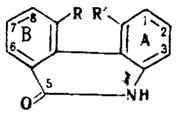
The corresponding mono-, di-, and triamino derivatives substituted in the 2, 4, and 8 positions of the phenanthridone ring were obtained by reduction of mono-, di-, and trinitro-substituted phenanthridone (I), phenanthridone-10-carboxylic acid (II), phenanthridone-1-carboxylic acid (III), 4H-cyclopenta[k,l,m]phenanthridine-5,9-dione (IV), 4H-cyclopenta[k,l,m]phenanthridin-5-one (V), 5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VI), and 5,9-dioxo-4,5,9,10-tetrahydro-4,10-diazapyrene (VII) with powdered iron in an electrolyte medium, with hydrogen in the presence of a nickel catalyst, or with stannous chloride. The 2,4,7,9-tetraamino derivative of VI was similarly obtained. 1-Amino-, 7-amino-, and 10-aminophenanthridones were obtained by the Schmidt reaction from the corresponding carboxylic acids. 1,10-Diamino- and 3,8-diaminophenanthridones were similarly obtained from the corresponding aminofluorenones.

Continuing our research on intermediates for dyes and monomers for polymeric materials we synthesized a number of amino derivatives of phenanthrodone (I) [2], phenanthridone-10-carboxylic acid (II) [3], phenanthridone-1-carboxylic acid (III) [4], 4H-cyclopenta[k,l,m]-phenanthridine-5,9-dione (IV) [5], 4H-cyclopenta[k,l,m]phenanthridin-5-one (V) [6], 5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VI) [7], and 5,9-dioxo-4,5,9,10-tetrahydro-4,10-diazapyrene (VII) [3].



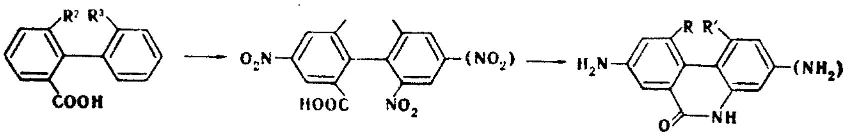
I-III



IV-VII

I $R=R'=H$; II $R=COOH$, $R'=H$; III $R=H$, $R'=COOH$; IV $R+R'=CO$; V $R+R'=CH_2$; VI $R+R'=NHCO$; VII $R+R'=CONH$

Several mono- and diamino-substituted derivatives (I-VII*l*, I-VIIm) of I-VII were previously obtained [2-6] by nitration of carboxylic acids VIII-XII to di-, tri-, or tetranitro-substituted compounds and subsequent reduction of the nitro compounds:



VIII-XII

I-VII l,m

VIII $R^2=R^3=H$; IX $R^2=COOH$, $R^3=H$; X $R^2=H$, $R^3=COOH$; XI $R^2+R^3=CO$; XII $R^2+R^3=CH_2$

The nitration of carboxylic acids VIII-XII takes place in the ortho and para positions of the biphenyl ring. In the case of reduction of the nitro-substituted compounds with $NO_2$ groups in the ortho position to $NH_2$ groups the latter undergo cyclization with the COOH

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*See [1] for Communication 3.

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TABLE 1. Amino-Substituted Phenanthridones and Phenanthridone Derivatives

| Com-pound | R | R′ | Posi. of amino group | Meth. of prep. | IR spectra, cm$^{-1}$ (in KBr) | Found, % |  |  | Empirical formula | Calc., % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | or a gp. formed by R and R′ together |  |  |  |  | C | H | N |  | C | H | N |  |
| Ia* | H | H | 2 | B | 3400—3300 ($NH_2$), 3200—3050 (NH) | 74,2 | 4,9 | 13,2 | $C_{13}H_{10}N_2O$ | 74,3 | 4,8 | 13,3 | 72 |
| Ib* | H | H | 4 | B | 3440—3350 ($NH_2$), 3150—3000 (NH) | 74,4 | 5,0 | 13,2 | $C_{13}H_{10}N_2O$ | 74,3 | 4,8 | 13,3 | 70 |
| I c | H | H | 2, 8 | B | 3400—3350 ($NH_2$), 3150—3050 (NH) | 69,2 | 5,0 | 18,6 | $C_{13}H_{11}N_3O$ | 69,3 | 4,9 | 18,7 | 68 |
| I d | H | H | 4, 8 | B | 3450—3300 ($NH_2$), 3200—3050 (NH) | 69,3 | 5,1 | 18,5 | $C_{13}H_{11}N_3O$ | 69,3 | 4,9 | 18,7 | 65 |
| I e | H | H | 2, 4, 8 | B | 3440—3300 ($NH_2$), 3200—3000 (NH) | 64,8 | 5,2 | 23,2 | $C_{13}H_{12}N_4O$ | 65,0 | 5,0 | 23,3 | 63 |
| II a | COOH | H | 2 | A | 3480—3350 ($NH_2$), 3150—3050 (NH) | 66,0 | 4,0 | 10,8 | $C_{14}H_{10}N_2O_3$ | 66,1 | 3,9 | 11,0 | 85 |
| II b | COOH | H | 4 | A | 3470—3380 ($NH_2$), 3200—3070 (NH) | 66,1 | 4,1 | 10,9 | $C_{14}H_{10}N_2O_3$ | 66,1 | 3,9 | 11,0 | 80 |
| III a | H | COOH | 2 | A | 3450—3350 ($NH_2$), 3200—3080 (NH) | 66,0 | 3,9 | 10,9 | $C_{14}H_{10}N_2O_3$ | 66,1 | 3,9 | 11,0 | 85 |
| III b | H | COOH | 4 | A | 3460—3300 ($NH_2$), 3200—3000 (NH) | 65,9 | 4,0 | 11,0 | $C_{14}H_{10}N_2O_3$ | 66,1 | 3,9 | 11,0 | 80 |
| III c | H | COOH | 2, 4, 8 | A | 3440—3350 ($NH_2$), 3200—3050 (NH) | 59,1 | 4,3 | 19,8 | $C_{14}H_{12}N_4O_3$ | 59,2 | 4,2 | 19,7 | 81 |
| IVa† | —CO— |  | 1 | B | 3400—3300 ($NH_2$), 3060 (NH) 1695 (CO), 1665 (CONH) | 71,1 | 3,5 | 11,8 | $C_{14}H_8N_2O_2$ | 71,2 | 3,4 | 11,9 | 68 |
| IVb† | —CO— |  | 3 | B | 3440—3300 ($NH_2$), 3150—3000 (NH), 1690 (CO), 1665 (CONH) | 71,0 | 3,4 | 11,8 | $C_{14}H_8N_2O_2$ | 71,2 | 3,4 | 11,9 | 63 |
| IVc† | —CO— |  | 1, 7 | B | 3440—3350 ($NH_2$), 3150—3070 (NH), 1695 (CO), 1660 (CONH) | 66,7 | 3,7 | 16,6 | $C_{14}H_9N_3O_2$ | 66,9 | 3,6 | 16,7 | 70 |
| IVd† | —CO— |  | 3, 7 | B | 3450—3350 ($NH_2$), 3200—3050 (NH), 1695 (CO), 1665 (CONH) | 66,8 | 3,8 | 16,7 | $C_{14}H_9N_3O_2$ | 66,9 | 3,6 | 16,7 | 65 |
| IVe† | —CO— |  | 1, 3, 7 | B | 3450—3300 ($NH_2$), 3200—3000 (NH), 1695 (CO), 1665 (CONH) | 63,1 | 3,9 | 20,9 | $C_{14}H_{10}N_4O_2$ | 63,2 | 3,8 | 21,0 | 60 |
| V a | —$CH_2$— |  | 1 | C | 3400—3300 ($NH_2$), 3150—3000 (NH), 1665 (CONH) | 75,6 | 4,4 | 12,7 | $C_{14}H_{10}N_2O$ | 75,7 | 4,5 | 12,6 | 80 |
| V b | —$CH_2$— |  | 3 | C | 3440—3300 ($NH_2$), 3200—3000 (NH), 1660 (CONH) | 75,8 | 4,6 | 12,6 | $C_{14}H_{10}N_2O$ | 75,7 | 4,5 | 12,6 | 82 |
| V c | —$CH_2$— |  | 1, 7 | C | 3440—3340 ($NH_2$), 3150—3000 (NH), 1665 (CONH) | 71,0 | 4,7 | 17,6 | $C_{14}H_{11}N_3O$ | 70,9 | 4,6 | 17,7 | 80 |
| V d | —$CH_2$— |  | 3, 7 | C | 3450—3300 ($NH_2$), 3150—3000 (NH), 1665 (CONH) | 70,9 | 4,6 | 17,8 | $C_{14}H_{11}N_3O$ | 70,9 | 4,6 | 17,7 | 85 |
| V e | —$CH_2$— |  | 1, 3, 7 | C | 3460—3300 ($NH_2$), 3150—3000 (NH), 1660 (CONH) | 66,6 | 4,9 | 22,0 | $C_{14}H_{12}N_4O$ | 66,7 | 4,8 | 22,2 | 80 |
| VI a | —HN—CO— |  | 1 | B | 3460—3350 ($NH_2$), 3150—3050 (NH), 1660 (CONH) | 67,0 | 3,7 | 16,6 | $C_{14}H_9N_3O_2$ | 66,9 | 3,6 | 16,7 | 68 |
| VI b | —HN—CO— |  | 3 | B | 3450—3400 ($NH_2$), 3100—3000 (NH), 1650 (CONH) | 66,9 | 3,6 | 16,7 | $C_{14}H_9N_3O_2$ | 66,9 | 3,6 | 16,7 | 70 |
| VI c | —HN—CO— |  | 1, 8 | B | 3440—3350 ($NH_2$), 3150—3050 (NH), 1655 (CONH) | 63,1 | 3,9 | 20,9 | $C_{14}H_{10}N_4O_2$ | 63,2 | 3,8 | 21,0 | 65 |
| VI d | —HN—CO— |  | 1, 3, 6 | B | 3440—3350 ($NH_2$), 3100—3000 (NH), 1660 (CONH) | 59,7 | 4,0 | 24,8 | $C_{14}H_{11}N_5O_2$ | 59,8 | 3,9 | 24,9 | 63 |
| VI e | —HN—CO— |  | 1, 3, 8 | B | 3450—3350 ($NH_2$), 3200—3080 (NH), 1660 (CONH) | 59,8 | 4,0 | 24,8 | $C_{14}H_{11}N_5O_2$ | 59,8 | 3,9 | 24,9 | 71 |
| VI f | —HN—CO— |  | 1, 3, 6, 8 | B | 3440—3300 ($NH_2$), 3200—3000 (NH), 1665 (CONH) | 56,7 | 4,2 | 28,3 | $C_{14}H_{12}N_6O_2$ | 56,8 | 4,0 | 28,4 | 62 |
| VII a | —OC—NH— |  | 1 | D | 3440—3350 ($NH_2$), 3150—3000 (NH), 1665 (CONH) | 66,9 | 3,8 | 16,7 | $C_{14}H_9N_3O_2$ | 66,9 | 3,6 | 16,7 | 51 |
| VII b | —OC—NH— |  | 1, 3 | D | 3450—3300 ($NH_2$), 3200—3050 (NH), 1660 (CONH) | 63,0 | 4,0 | 24,9 | $C_{11}H_{10}N_4O_2$ | 63,2 | 3,8 | 21,0 | 49 |
| VII c | —OC—NH— |  | 1, 3, 7 | D | 3420—3350 ($NH_2$), 3200—3000 (NH), 1660 (CONH) | 59,8 | 4,0 | 25,0 | $C_{14}H_{11}N_5O_2$ | 59,8 | 3,9 | 24,9 | 45 |

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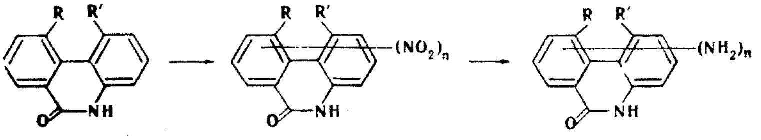
*Compound Ia had mp 286°C (mp 285°C [8]). Compound Ib had mp 264°C (dec.).

†The compounds were synthesized by N. G. Grekhova[1].

groups of the adjacent benzene ring to give one or two α-pyridone rings that are condensed in the o,o' positions of the biphenyl ring. However, only mono- and diamino derivatives of I-VII that are substituted in the para positions relative to the biphenyl C—C' bond were obtained via this scheme.

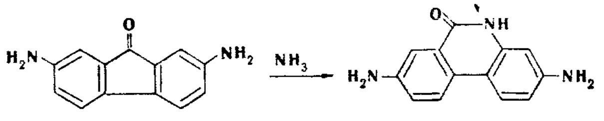
In order to obtain amino derivatives of I-III that are substituted in the 2,4, and 8 positions and amino derivatives of IV-VII that are substituted in the 1, 3, and 7 positions, respectively, we proposed the scheme



I-VII n=1-4 I, IV, Va-e IIa,b
III, VIIa-c VIa-f

Mono-, di-, and trinitro-substituted compounds were obtained via this scheme by nitration of I-VII. A tetranitro-substituted compound was obtained in the case of VI. The orientation of the substituents in the nitration of I-VII is determined by the presence in them of a phenanthridone system [1] rather than by a biphenyl ring, as in the case of the nitration of VIII-XII. The preparation and isolation of nitro-substituted derivatives of I-VII were described in the preceding communication [1]. The reduction of the nitro compounds was carried out with powdered iron in a medium consisting of ammonium hydroxide and ammonium chloride (Method A), with powdered iron in aqueous dioxane or DMF (Method B), with hydrogen under pressure over Raney nickel (Method C), or with stannous chloride in acetic and hydrochloric acids (Method D). We obtained a number of amino compounds via the second scheme (see Table 1).

1-Amino-, 10-amino-, and 9-aminophenanthridones (If-h) cannot be obtained via the schemes examined above. These amines were obtained from, respectively, III, II, and phenanthridone-9-carboxylic acid (XIII) by replacement of the COOH groups by $NH_2$ groups via the Schmidt reaction. 3,8-Diaminophenanthridone (Ii) was also obtained via the Schmidt reaction by treatment of 2,7-diaminofluorenone (XIV) with sodium azide in sulfuric acid. Expansion of the five-membered ring that contains a keto group to give a six-membered α-pyridone ring occurs under these conditions:



XIV Ii

1,10-Diaminophenanthridone (Ij) was similarly obtained from 4,5-diaminofluorenone (XV).

The position of the absorption bands of the CONH, $NH_2$, and CO groups in the IR spectra of crystalline amino-substituted derivatives of I-VII provides a basis for the assumption that the CO (ketone and amide), NH, and $NH_2$ groups are associated. Thus the absorption band of the keto group for IV was at 1724 cm$^{-1}$. In the case of all of the amino-substituted derivatives of IV it is shifted to the shorter-wave region (1690-1695 cm$^{-1}$). These data indicate the existence of intermolecular CO...$H_2N$ bonds in these compounds. The intermolecular hydrogen bonds are the reason for the low solubility of the amino-substituted compounds in organic solvents. As a rule, they melt below 350°C and become darker and undergo decomposition at higher temperatures. Analytical samples of the amines were obtained by sublimation at 310-360°C and a residual pressure of up to 10$^{-3}$ mm and by recrystallization from DMF. All of the amino-substituted compounds fluoresce upon irradiation with UV light.

## EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were measured with a UR-20 spectrometer.

Reduction of Nitro-Substituted Compounds I-VII. A) A 7.5-g (0.13 mole) sample of powdered iron was added to a flask containing 30 ml of a 3% aqueous solution of ammonium chloride, a solution of 0.01 mole of nitro-substituted II or III in 30 ml of 10% ammonium hydroxide was added with vigorous stirring, and the mixture was heated on a boiling-water bath for 50 min. It was then treated with 40 ml of 20% alkali, and the solution was filtered.

The precipitate was washed several times with alkali, and the filtrates were combined and neutralized to pH 7. The precipitate was removed by filtration, washed with water, and dried.

B) A 7.5-g (0.13 mole) sample of iron powder was added to a flask containing 30 ml of a 3% aqueous solution of ammonium chloride, the flask was heated on a water bath, and a solution of 0.01 mole of nitro-substituted I-VII in 40 ml of dioxoane or DMF was added with vigorous stirring in the course of 10 min. The mixture was stirred for 40 min, and the amine was then isolated by extraction with refluxing solvent.

C) A 0.01-mole sample of nitro-substituted V in 60 ml of dioxane or DMF was added to a 200 ml autoclave, 1.2 g of Raney nickel was added, and a hydrogen pressure of 50 atm was created. The mixture was stirred vigorously at 110°C for 4 h. The amine was then separated from the catalyst.

D) A 0.01-mole sample of nitro-substituted VII was added to a flask containing 60 ml of acetic acid and 20 ml of concentrated hydrochloric acid, the flask was heated on a boiling-water bath, and 17 g (0.07 mole) of stannous chloride in 30 ml of hydrochloric acid was added in the course of 10 min. The mixture was heated on a water bath for 1 h, after which the precipitate was removed by filtration and dissolved in sulfuric acid, and the solution was poured over ice. The amine sulfate was converted to the base by heating in 10% alkali. The product was removed by filtration, washed, and dried.

1-Aminophenanthridone (If). A 2.7-g (0.01 mole) sample of acid III was dissolved in 45 ml of 94% sulfuric acid, 0.71 g (0.011 mole) of sodium azide was added in portions, and the mixture was stirred for 1 h and poured over ice. Workup gave 2 g (90%) of If with mp 323-324°C (from dioxane) [8].

9-Aminophenanthridone (Ih). This compound, with mp 285-286°C (from dioxane) [8], and 10-aminophenanthridone (Ig), with mp 334-335°C (from dioxane) [8], were similarly obtained from carboxylic acids XIII and II, respectively, in 90-92% yields.

1,10-Diaminophenanthridone (Ij). A 2.71-g (0.01 mole) sample of diamine XV was dissolved in 50 ml of 94% sulfuric acid, 0.71 g (0.011 mole) of sodium azide was added in portions, and the mixture was stirred for 2 h and poured over ice. Workup gave 2.42 g (85%) of Ij with mp > 330°C (dec.). Found: C 69.5; H 5.0; N 18.8%. $C_{13}H_{11}N_3O$. Calculated: C 69.3; H 4.9; N 18.7%.

3,8-Diaminophenanthridone (Ii). This compound, with mp > 330°C (from DMF), was similarly obtained in 85% yield from diamine XIV. Found: C 69.4; H 5.1; N 18.9%. $C_{13}H_{11}N_3O$. Calculated: C 69.3; H 4.9; N 18.7%.

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