2-Dicyanomethylene-1,3-dithiolane.—Ethylene trithiocarbonate (0.68 g, 0.005 mole) and 1.15 g (0.005 mole) of 2,2-dicyano-3,3-bis(trifluoromethylene)oxirane were dissolved in 15 ml of ether, and the solution was allowed to remain at room temperature overnight. The yellow solid that precipitated was collected on a filter and washed with ether. Recrystallization from alcohol gave 0.59 g of 2-dicyanomethylene-1,3-dithiolane as colorless plates, mp 202–203°. The infrared spectrum agreed with that of an authentic sample prepared by another method.[9]

(9) R. Gompper and W. Toepfl, *Ber.*, **95**, 2861 (1962).

Linear Indanthrone and Related Phenazines[1]

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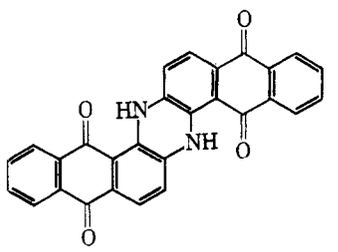
7,16-Dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine-5,9,14,18-tetrone (linear indanthrone) has been prepared by two unrelated methods. Examination of the properties of this substance and its derivatives indicates that the previously described syntheses of linear indanthrone have not afforded authentic material. Naphtho[2,3-*b*]-phenazine and several of its derivatives which are similar chemically and physically to linear indanthrone are described.

Indanthrone (**1**), which was discovered by Bohn[3] in 1901, is an important blue vat dye, and its chemistry has been extensively investigated.[4] However when we started our work little was known about the linear isomer of indanthrone, 7,16-dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine-5,9,14,18-tetrone (**2**), and we consider that the reported syntheses[5] of this compound have not yielded authentic material. Schiedt[5a] claimed to have obtained **2** by the reaction of formamide with hystazarinquinone (anthracene-2,3,9,10-tetrone) at 130°. The product was obtained as dark brown rods from quinoline, melting above 400°. A correct nitrogen analysis was reported, but no other properties were described. Attempts to repeat this reaction have been unsuccessful.[5c] Clark reported the synthesis of **2** by heating 2-amino-3-bromoanthraquinone with potassium carbonate, and also by the condensation of 2,3-diaminoanthraquinone with either 2,3-dibromoanthraquinone or hystazarinquinone.[5c] The linear indanthrone was reported to be a reddish brown compound which could not be crystallized from any organic solvent. Unsatisfactory analyses for carbon content were attributed to the hygroscopic nature of the product. No derivatives of the linear indanthrone were described.



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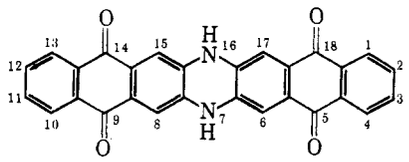

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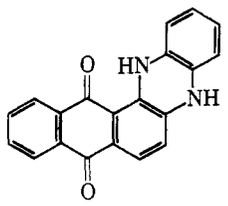

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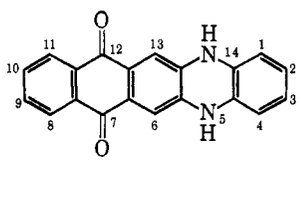

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5,14-Dihydronaphtho[2,3-*a*]phenazine-8,13-dione (**3**) is a blue substance having properties very similar to indanthrone.[6] Thus, as a preliminary to the unambiguous synthesis of linear indanthrone, we prepared 5,-14-dihydronaphtho[2,3-*b*]phenazine-7,12-dione (**4**) since we anticipated that this compound would resemble the linear indanthrone **2** in its physical and chemical properties.[7] 2-Bromo-3-nitroanthraquinone[8] was condensed with *o*-nitroaniline in boiling *o*-dichlorobenzene in the presence of lead oxide and cupric acetate affording the orange 2-(*o*-nitroanilino)-3-nitroanthraquinone (**5**). Reduction of this compound with sodium sulfide in ethanol afforded a mixture of the green dihydrophenazine **4** and 2-(*o*-aminoanilino)-3-aminoanthraquinone (**6**). Oxidation of compound **6** with ferric chloride in hydrochloric acid yielded the yellow naphtho[2,3-*b*]-phenazine-7,12-dione (**7**). A small yield of the phenazine **7** was also obtained by reaction of 2,3-diaminoanthraquinone with *o*-benzoquinone in warm acetic acid. A much better yield of the 1,2,3,4-tetrachloro derivative of **7** was obtained by reaction of 2,3-diaminoanthraquinone with the more stable 3,4,5,6-tetrachloro-*o*-benzoquinone. Treatment of the phenazine **7** with an alkaline solution of sodium hydrosulfite afforded a reddish brown vat, which on oxidation with air yielded the green dihydrophenazine **4**. The phenazine **7** was also obtained by oxidation of 5,14-dihydro-

(1) This investigation was supported by a Research Grant CA-5336 from the U. S. Public Health Service, and by Grant No 696-A from the Petroleum Research Fund of the American Chemical Society.

(2) (a) Alfred P. Sloan Foundation Fellow, 1963–1966; (b) National Science Foundation Predoctoral Fellow, 1962–1963.

(3) R. Bohn, German Patent 129,845–129,848; *Frdl.*, **6**, 412 (1900–1902); *Ber.*, **43**, 987 (1910).

(4) (a) G. A. Swan and D. G. I. Felton, "Phenazines," Interscience Publishers, Inc., New York, N. Y., 1957, p 264; (b) J. Weinstein and C. Merritt, *J. Am. Chem. Soc.*, **81**, 3759 (1959).

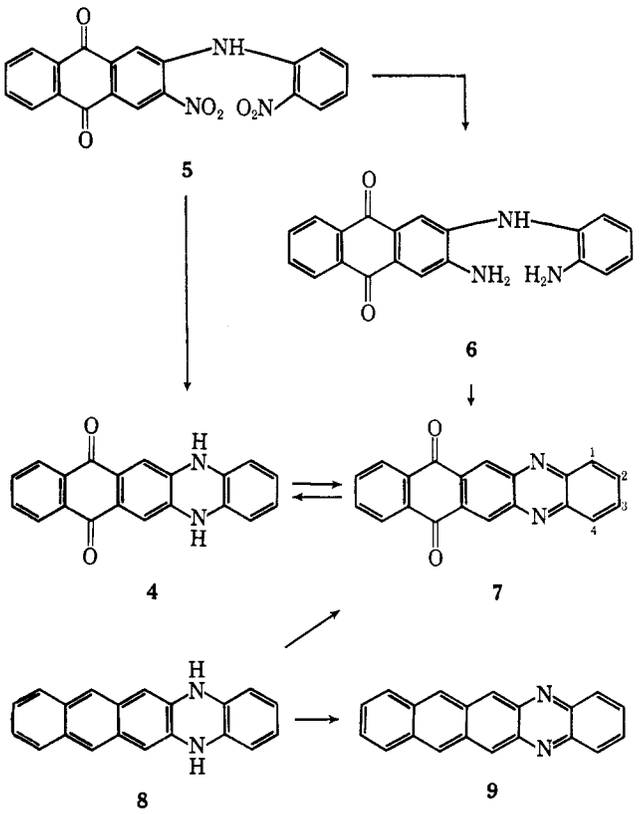
(5) (a) B. Schiedt, *J. Prakt. Chem.*, **157**, 203 (1941); (b) W. Bradley and M. C. Clark, *Chem. Ind.* (London), 1601 (1959); (c) M. C. Clark, *J. Chem. Soc.*, 277 (1966).

(6) F. Ullmann and O. Fodor, *Ann.*, **380**, 324 (1911).

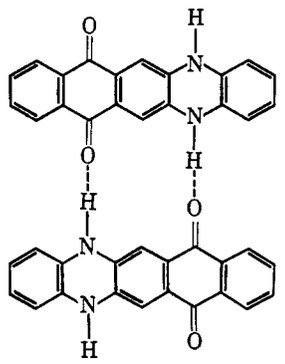
(7) The only reported representatives of this ring system are 7,12-diphenyl-5,14-dihydronaphtho[2,3-*b*]phenazine [A. Etienne and J. Bourdon, *Bull. Soc. Chim. France*, 380 (1955)] and naphtho[2,3-*b*]phenazine-6,13-dione [R. Wittig, H. Härle, E. Knauss, and K. Niethammen, *Ber.*, **93**, 951 (1960)].

(8) W. L. Mosby and W. L. Berry, *Tetrahedron*, **5**, 93 (1959).

SCHEME I



naphtho[2,3-*b*]phenazine (**8**) with sodium dichromate in acetic acid. Fusing a mixture of 2,3-dihydroxyanthracene with *o*-phenylenediamine afforded **8** (see Scheme I). Oxidation of dihydrophenazine **8** with cupric acetate in pyridine[9] yielded the parent substance of this series of compounds, naphtho[2,3-*b*]phenazine (**9**), which is greenish blue in color. The linear dihydrophenazine **4** is a bright green compound, very sparingly soluble in organic solvents (much less than its angular isomer **3**). This insolubility may be attributed to strong intermolecular hydrogen bonds, the C=O and NH groups being ideally situated for such bonding as illustrated in structure **10**. Thus the N,N′-dimethyl



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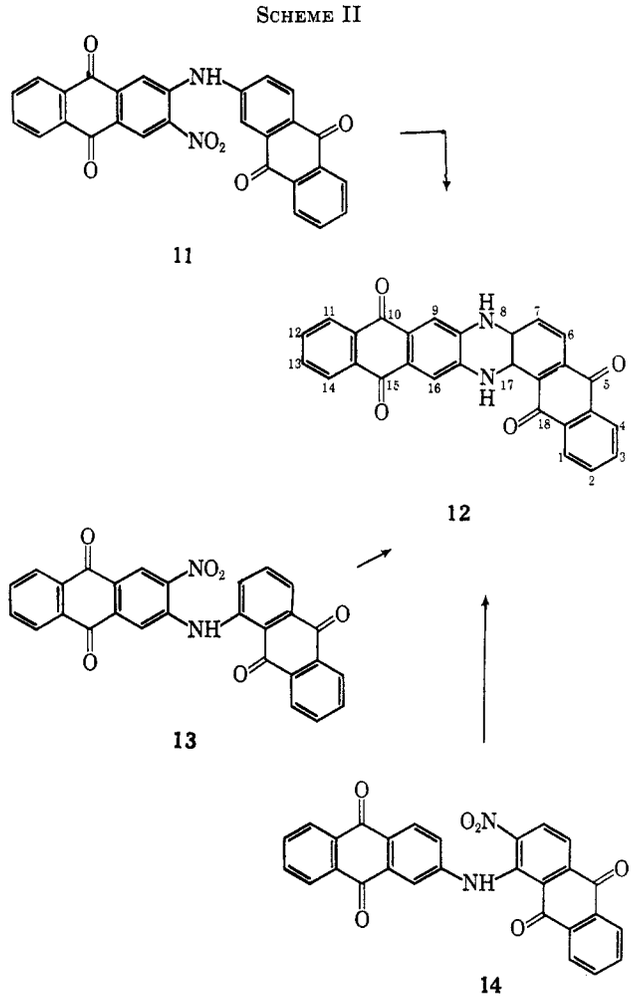
derivative, obtained by treatment of **4** with methyl *p*-toluenesulfonate in the presence of potassium carbonate, is readily soluble in organic solvents. Oxidation of the dihydrophenazine **4** with nitric acid in a mixture of acetic acid and acetic anhydride afforded the phenazine **7**, which was also more soluble in organic solvents. Some dehydrogenation of **4** also occurred on sublimation at 320°.

Our first attempted synthesis of linear indanthrone involved the condensation of 2-aminoanthraquinone with 2-bromo-3-nitroanthraquinone to yield 3-nitro-2,2′-dianthraquinonylamine (**11**). Reduction of this compound with alcoholic sodium sulfide did not yield the desired linear indanthrone, but an angular isomer, 8,17-dihydrodinaphtho[2,3-*a*:2′,3′-*i*]phenazine-5,10,15,-18-tetrone (**12**, see Scheme II) previously obtained by a similar reduction[10] of 2-nitro-1,2′-dianthraquinonylamine (**14**). This indanthrone isomer was also obtained by the sodium sulfide reduction of 3-nitro-2,1′-dianthraquinonylamine (**13**). 3,3′-Dinitro-2,2′-dianthra-

SCHEME II

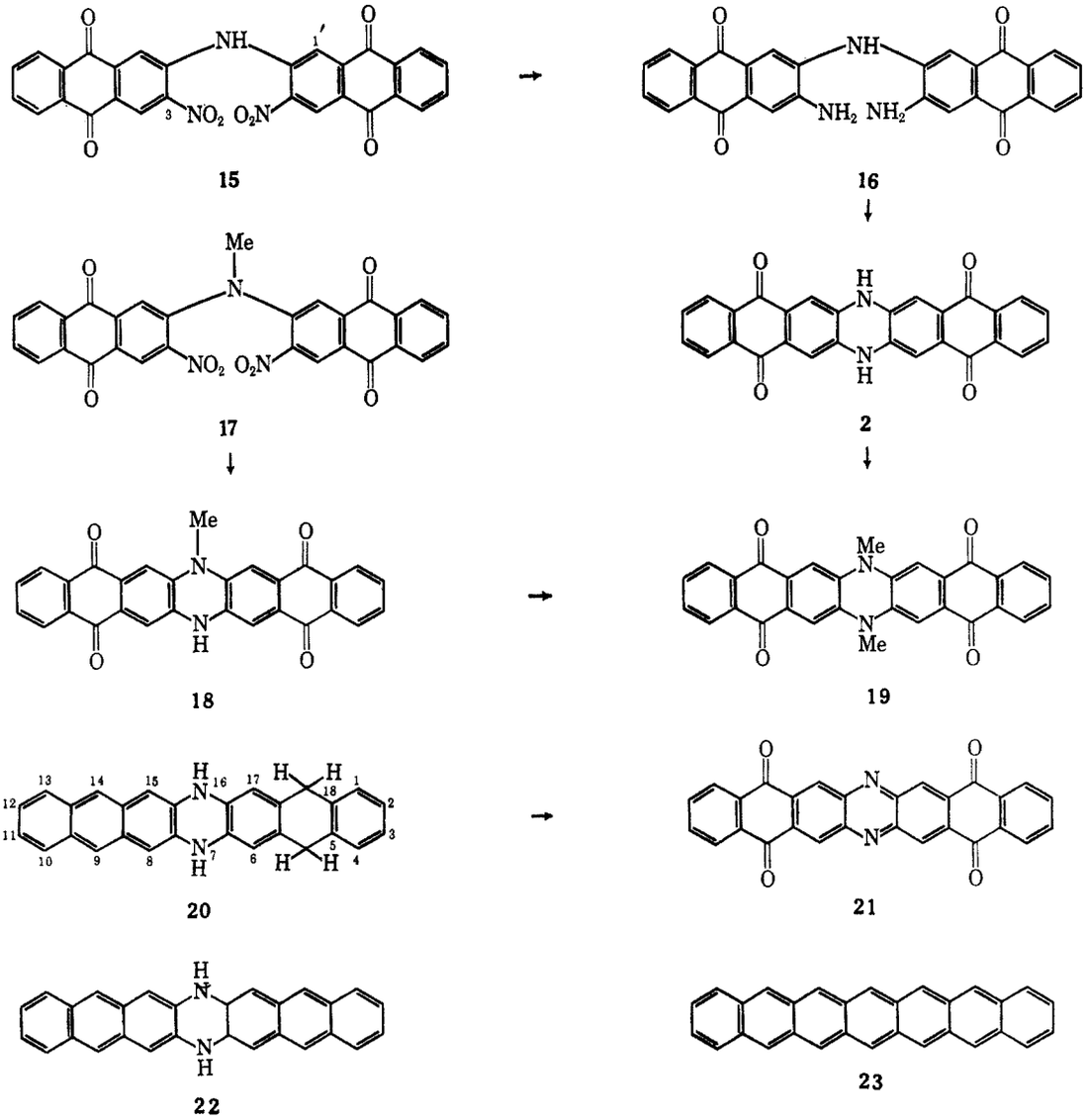


quinonylamine (**15**) was obtained by a condensation between 2-bromo-3-nitroanthraquinone and 2-amino-3-nitroanthraquinone. Reduction of this dinitro compound with alcoholic sodium sulfide yielded a deep blue mixture of products which could not be purified. We suspect that this reaction product contained 7-amino or 7-nitro derivatives of the indanthrone isomer **12**, the 3-nitro group in compound **15** having cyclized on the 1′ position of the other anthraquinonyl residue. Reduction of **15** with stannous chloride in a mixture of hydrochloric and acetic acid gave a purple compound, presumably 3,3′-diamino-2,2′-dianthraquinonylamine

(9) This reagent was previously used for the oxidation of 6,13-dihydrodibenzo[*b*,*i*]phenazine to the corresponding phenazine: J. A. VanAllan, R. E. Adel, and G. A. Reynolds, *J. Org. Chem.*, **27**, 2873 (1962).

(10) W. Bradley, E. Leete, and D. S. Stephens, *J. Chem. Soc.*, 2163 (1951).

SCHEME III



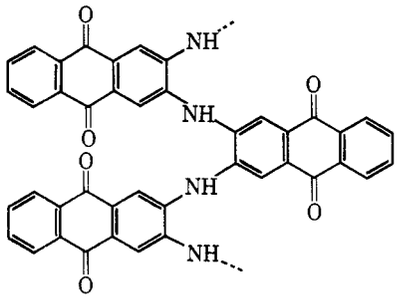
(16, Scheme III). Oxidation of this compound with ferric chloride yielded the linear indanthrone **2** as a dark green compound. It gave a reddish brown vat on reduction with alkaline sodium hydrosulfite, the linear indanthrone being regenerated on air oxidation. Oxidation with nitric acid in boiling acetic acid yielded the yellow azine **21**, which was readily crystallized from *o*-nitroanisole or N,N-dimethylformamide. By passing hydrogen into a solution of this azine in boiling quinoline the linear indanthrone **2** was obtained crystalline, and this material analyzed correctly for carbon, hydrogen, nitrogen. Its mass spectrum had a molecular ion peak at *m/e* 442 corresponding to structure **2**. Methylation of the dinitro compound **15** with methyl-*p*-toluene sulfonate yielded N-methyl-3,3′-dinitro-2,2′-dianthraquinonylamine (**17**). Reduction of this compound with stannous chloride, followed by oxidation with ferric chloride yielded linear N-methylindanthrone (**18**), which was soluble in boiling quinoline and could be crystallized from this solvent. Methylation yielded linear N,N′-dimethylindanthrone (**19**) which was also obtained by the direct methylation of linear indanthrone. All these compounds analyzed correctly and had the expected molecular ion peaks in their mass mass spectra.

We also obtained linear indanthrone by making use of Bollert's reaction.[11] He obtained 2,2′-dianthrylamine by refluxing 2-aminoanthracene in acetic acid. In contrast with the experience of Clark[5c] we found no difficulty in obtaining a good yield of 2,3-diaminoanthracene by the reduction of 2,3-diaminoanthraquinone with zinc in 5% sodium hydroxide. On refluxing 2,3-diaminoanthracene in *o*-dichlorobenzene with a small amount of acetic acid a bright yellow solid was deposited which analyzed for $C_{28}H_{20}N_2$ instead of the expected $C_{28}H_{18}N_2$ for 7,16-dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine (**22**). However it is well known that the analogous linear polynuclear hydrocarbons readily form hydro derivatives. Thus it was not possible to obtain pure heptacene (**23**) by dehydrogenation of its hydro derivatives with palladium on charcoal.[12] The extra hydrogens are tentatively assigned to the 5,18 positions (**20**). Treatment of this condensation product with methyl *p*-toluenesulfonate in boiling *o*-dichlorobenzene in the presence of potassium carbonate yielded a product which is apparently the N,N′-dimethyl derivative of **22**, since its mass spectrum had a molecular ion peak at *m/e* 410.

(11) A. Bollert, *Ber.*, **16**, 1635 (1883).
(12) B. Boggiano and E. Clar, *J. Chem. Soc.*, 2681 (1957).

Oxidation of **20** with sodium dichromate in acetic acid yielded the azine **21**, which on reduction yielded linear indanthrone, identical with the previously obtained material.

We suggest that the material obtained by Clark[5c] by the self-condensation of 2-amino-3-bromoanthraquinone is polymeric, having a partial structure such as **24**. Its reported properties are consistent with this



24

structure. 2,2′-Dianthraquinonylamine is reddish brown[13] and, like the compound obtained by Clark, forms a relatively stable salt with methanolic potassium hydroxide.

Experimental Section

General Methods.—Melting points are corrected. Ultraviolet and visible spectra were determined using a Beckman Model DK-2 or a Cary 11 spectrophotometer with acetonitrile as a solvent except where noted. Ultraviolet and visible spectra of many of the anthraquinone derivatives described could not be obtained because of their low solubility in organic solvents at room temperature. Infrared spectra were determined in potassium bromide pellets on a Perkin-Elmer Model 21 spectrophotometer. Mass spectra were determined by Mr. Adrian Swanson on an Hitachi-Perkin-Elmer Model RMU mass spectrometer with a direct inlet system. Microanalyses were determined by Mrs. Olga Hamerston, Mr. T. S. Prokopov, and their assistants at the University of Minnesota. The acidic character of aminoanthraquinones and their derivatives can be readily demonstrated by the addition of a 56% solution of potassium hydroxide in methanol to a pyridine solution of the anthraquinone.[14] In most cases a marked color change is observed in the color of the solution, and the change is reversed on the addition of water or ethanol, immediately when the derivative is a weak acid less readily when it is stronger.

2-(*o*-Nitroanilino)-3-nitroanthraquinone (5).—2-Bromo-3-nitroanthraquinone[15] (13.5 g), *o*-nitroaniline (9.0 g), lead monoxide (litharge, 9.0 g), and cupric acetate monohydrate (0.3 g) were refluxed with stirring in *o*-dichlorobenzene (90 ml) for 14 hr. The mixture was filtered hot and the filtrate on cooling deposited the crude product (12.1 g). Recrystallization from nitrobenzene afforded orange plates (7.2 g) of **5**, mp 279–280°; infrared spectrum showed ν_{max} 3360 (NH) and 1680 cm^{-1} (C=O). It dissolves in concentrated sulfuric acid with a violet-red color. Its orange solution in pyridine becomes violet on addition of methanolic potassium hydroxide.

Anal. Calcd for $C_{20}H_{11}N_3O_6$: C, 61.70; H, 2.85; N, 10.79. Found: C, 61.66; H, 2.61; N, 10.86.

Reduction of the Dinitro Compound 5.—Compound **5** (8.0 g) was refluxed in 90% ethanol (500 ml) containing sodium sulfide enneahydrate (30 g) for 24 hr. The mixture was filtered hot and the dried residue (5.0 g) was extracted with boiling nitrobenzene. A bright green residue (0.9 g) remained, which on crystallization from quinoline yielded emerald green prisms of **5,14-dihydronaphtho[2,3-*b*]phenazine-7,12-dione (4)**, whose infrared spectrum showed ν_{max} 3340 (NH) and 1649 cm^{-1} (C=O). It gives a yellowish brown color in concentrated sulfuric acid. It dissolves slightly in cold pyridine with a greenish yellow color becoming blue on the addition of methanolic potassium hydroxide. On sublimation (320° at 0.001 mm) in a glass tube, two zones were produced. The more volatile yellow zone was the phenazine **7**, described in the following section. The less volatile zone was the greenish blue dihydrophenazine **4**. On attempting to determine the melting point of **4** dehydrogenation occurred and the yellow phenazine **7**, mp 402–403°, was obtained.

Anal. Calcd for $C_{20}H_{12}N_2O_2$: C, 76.91; H, 3.87; N, 8.79. Found: C, 77.20; H, 4.05; N, 8.80.

The nitrobenzene extract on cooling deposited violet-red needles of **2-(*o*-aminoanilino)-3-aminoanthraquinone (6, 3.8 g)**, mp 293–294°. It dissolves in concentrated sulfuric acid with a violet color. Its red solution in pyridine becomes dull green on the addition of methanolic potassium hydroxide.

Anal. Calcd for $C_{20}H_{15}N_3O_2$: C, 72.93; H, 4.49; N, 12.76. Found: C, 72.80; H, 4.67; N, 12.49.

Naphtho[2,3-*b*]phenazine-7,12-dione (7). A. From the Dihydrophenazine.—The dihydrophenazine **4** (100 mg) was suspended in a mixture of boiling acetic acid (40 ml) and acetic anhydride (40 ml) to which was added 3 drops of concentrated nitric acid. The mixture became yellow, and after 30 min a clear solution was obtained. On cooling yellow needles of naphtho[2,3-*b*]-phenazine-7,12-dione (56 mg), mp 402–403°, separated. Its infrared spectrum had no absorption in the NH region and a C=O absorption at 1680 cm^{-1}. It dissolves in concentrated sulfuric acid with a reddish brown color.

Anal. Calcd for $C_{20}H_{10}N_2O_2$: C, 77.41; H, 3.25; N, 9.03. Found: C, 77.43; H, 3.14; N, 8.97.

The phenazine **7** (70 mg) was warmed with a solution of sodium hydroxide (0.3 g) and sodium hydrosulfite (0.3 g) in water (10 ml) when a reddish brown solution was obtained. Oxygen was bubbled through this solution. A transient deep blue color was observed which changed to green on further oxygenation. The green precipitate was filtered off and sublimed *in vacuo* when two zones were obtained, a yellow one of the phenazine **7**, and a greenish blue one of the dihydrophenazine **4** (31 mg).

B. From 2-(*o*-Aminoanilino)-3-aminoanthraquinone (6).—The amino compound **6** (3.0 g) was suspended in 300 ml of 20% hydrochloric acid and ferric chloride hexahydrate (100 g) added. The mixture was stirred on a steam bath for 16 hr, and then added to 2 l. of water. The pale, greenish yellow precipitate was filtered off and washed with sodium acetate solution, hot water, and ethanol. The residue was crystallized from nitrobenzene (charcoal) affording the phenazine **7** (1.5 g) identical (infrared spectrum) with the previously described material.

C. From 2,3-Diaminoanthraquinone.—2,3-Diaminoanthraquinone[16] (238 mg, 1 mmole) was added to a solution of *o*-benzoquinone[17] (250 mg, 2.5 mmoles) in acetic acid (100 ml) and the mixture was refluxed for 1 hr. The cooled solution was filtered and the filtrate was diluted with water (50 ml). On standing a brownish yellow precipitate separated. This material was removed by centrifuging, washed with water, and sublimed (300° at 0.01 mm) affording a yellow and a blue sublimate. The more volatile yellow sublimate was crystallized from *o*-dichlorobenzene to afford yellow needles of the phenazine **7** (52 mg).

On refluxing a mixture of 2,3-diaminoanthraquinone (238 mg, 1 mmole) with 3,4,5,6-tetrachloro-*o*-benzoquinone (246 mg, 1 mmole) in acetic acid (100 ml) for 1 hr a brownish yellow precipitate separated. Crystallization from nitrobenzene yielded hairlike yellow needles of **1,2,3,4-tetrachloronaphtho[2,3-*b*]-phenazine-7,12-dione (206 mg)**, mp >360°.

Anal. Calcd for $C_{20}H_6Cl_4N_2O_2$: C, 53.60; H, 1.35; N, 6.25. Found: C, 53.29; H, 1.59; N, 6.14.

5,14-Dimethyl-5,14-dihydronaphtho[2,3-*b*]phenazine-7,12-dione.—The dihydrophenazine **4** (0.5 g) was refluxed in *o*-dichlorobenzene (100 ml) with methyl *p*-toluenesulfonate (2 ml) in the presence of powdered potassium carbonate (1.5 g) for 16 hr. in a nitrogen atmosphere. The mixture was filtered hot. The filtrate was evaporated to 20 ml, diluted with benzene, and chromatographed on Woelm alumina (activity I). A strongly absorbed green zone was eluted with 40% chloroform in benzene. Evaporation of the green eluent yielded green needles of 5,-14-dimethyl-5,14-dihydronaphtho[2,3-*b*]phenazine-7,12-dione (70 mg), mp 308–309°, having no absorption in the NH region of the

(13) W. Bradley and E. Leete, *J. Chem. Soc.*, 2129 (1951).

(14) W. Bradley, *J. Soc. Dyers Colourists*, **58**, 2 (1942).

(15) We thank Dr. W. L. Mosby of American Cyanamid Co., Bound Brook, N. J., for the generous supply of 2-acetamido-3-bromoanthraquinone which was hydrolyzed with ethanolic sodium hydroxide yielding 2-amino-3-bromoanthraquinone which was oxidized with peracetic acid to afford the desired nitro compound.[8]

(16) R. Scholl and F. Kacer, *Ber.*, **37**, 4531 (1904).

(17) R. Willstäter and A. Pfannenstiel, *ibid.*, **37**, 4744 (1904).

infrared spectrum, and a C=O absorption at 1660 cm.$^{-1}$; ultraviolet spectrum (in 95% ethanol) at 245 mμ (log ε 4.71), 3.61 (4.40), 632 (3.09). It dissolves in pyridine with a beautiful green color and undergoes no color change on the addition of methanolic potassium hydroxide.

Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.82; H, 4.84; N, 8.10.

The residue from the initial filtration contained unmethylated phenazine **4** (280 mg).

5,14-Dihydronaphtho[2,3-*b*]phenazine (8).—2,3-Dihydroxyanthracene[18] (1.3 g) and *o*-phenylenediamine (10 g) were heated with stirring in a nitrogen atmosphere, the temperature being slowly raised from 180° to 225°. After 1 hr the cooled reaction product was washed with boiling ethanol and acetic acid leaving pale yellow plates of **8**: 0.95 g; 54%, mp >360°; λ_{max} 222 mμ (log ε 4.46), 240 (4.50), 273 (4.75), 308 (4.84), 326 (4.58); infrared spectrum, ν_{max}^{Nujol} 3360 cm^{-1} (NH). The analytical sample was crystallized from N,N-dimethylformamide.

Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.24; H, 4.81; N, 9.76.

It dissolves in concentrated sulfuric acid with an orange color. Its yellow solution in pyridine has an intense green fluorescence.

Sodium dichromate (200 mg) was added in small portions to a refluxing suspension of the phenazine **8** (100 mg) in acetic acid (5 ml). After 5 min the reaction mixture was added to water. The resultant precipitate was washed with water and sodium acetate solution, and crystallized from *o*-dichlorobenzene affording yellow needles of the phenazine **7** (80 mg), identical in all its properties with the previously described material.

Naphtho[2,3-*b*]phenazine (9).—A solution of cupric acetate monohydrate (300 mg) in pyridine (5 ml) was added to a suspension of the dihydrophenazine **8** (300 mg) in pyridine (100 ml), and the mixture was heated on a steam bath for 30 min while air was bubbled through the mixture. Methanol (300 ml) was then added and the residue obtained on filtration was sublimed (280° at 0.001 mm) affording dark green plates of naphtho[2,3-*b*]-phenazine: 25 mg; mp >360°; λ_{max} 223 mμ (log ε 4.46), 237.5 (4.49), 273 (4.56), 307 (4.65) (in acetonitrile), 409 (3.53), 4.33 (3.54), 582 (2.86) (in N,N-dimethylformamide); it has no absorption in the NH region of the infrared spectrum. It dissolves in concentrated sulfuric acid with a rose color which changes to orange on standing. It gives deep bluish green solutions in N,N-dimethylformamide and *o*-dichlorobenzene.

Anal. Calcd for $C_{20}H_{12}N_2$ (280): C, 85.69; H, 4.32. Found: C, 85.83; H, 4.42.

The mass spectrum had a molecular ion peak at *m/e* 280.

3-Nitro-2,2′-dianthraquinonylamine (11).—2-Aminoanthraquinone (1.12 g), 2-bromo-3-nitroanthraquinone (1.66 g), lead monoxide (2.0 g), and cupric acetate monohydrate (25 mg) were refluxed in *o*-dichlorobenzene (10 ml) for 4 hr. The mixture was then filtered hot and the filtrate deposited dark brown crystals (2.6 g), which were dissolved in chlorobenzene and chromatographed on alumina (activity II). An orange-brown zone was eluted with 10% acetone in chlorobenzene. Evaporation of the eluant yielded orange-brown needles of 3-nitro-2,2′-dianthraquinonylamine (420 mg). Recrystallization from nitrobenzene afforded orange prisms, mp >360°; infrared spectrum showed 3340 (NH) and 1675 cm^{-1} (C=O). It gives an intense bluish violet color in concentrated sulfuric acid. The yellow solution in pyridine becomes dull blue on addition of methanolic potassium hydroxide.

Anal. Calcd for $C_{28}H_{14}N_2O_6$: C, 70.89; H, 2.97; N, 5.91. Found: C, 70.56; H, 3.00; N, 5.85.

8,17-Dihydrodinaphtho[2,3-*a*:2′,3′-*i*]phenazine-5,10,15,18-tetrone (12).—The nitro compound **11** (47.4 mg) was refluxed in a solution of sodium sulfide enneahydrate (1.0 g) in 95% ethanol (50 ml) for 5 hr. The mixture became green almost immediately, and then greenish blue. The mixture was filtered and the residue was washed with water when it changed from greenish blue to bright blue. The crude product (30 mg) was crystallized from quinoline affording slate blue needles of the indanthrone isomer **12**, having an infrared spectrum identical with that of material previously obtained,[10] ν_{max} 3320 (NH) and 1665 cm^{-1} (C=O).

3-Nitro-2,1′-dianthraquinonylamine (13).—This compound was prepared by the condensation of 1-aminoanthraquinone with 2-bromo-3-nitroanthraquinone using the same experimental method as described for its isomer **11**. It was obtained as orange-red needles from nitrobenzene, mp >360°. It dissolves in concentrated sulfuric acid with a reddish blue color. Its orange solution in pyridine becomes deep violet on addition of methanolic potassium hydroxide.

Anal. Calcd for $C_{28}H_{14}N_2O_6$: C, 70.89; H, 2.97; N, 5.91. Found: C, 70.75; H, 2.97; N, 5.30.

Reduction of this compound with ethanolic sodium sulfide yielded the indanthrone isomer **12** in 74% yield.

3,3′-Dinitro-2,2′-dianthraquinonylamine (15).—2-Bromo-3-nitroanthraquinone (10 g), 2-amino-3-nitroanthraquinone[19] (10 g), lead monoxide (8 g), and powdered cupric acetate monohydrate (1.0 g) were refluxed in *o*-dichlorobenzene (200 ml) for 18 hr. The mixture was then cooled and the residue obtained on filtration was extracted with boiling *o*-nitroanisole (charcoal) yielding, on cooling, orange needles of 3,3′-dinitro-2,2′-dianthraquinonylamine (3.3 g), mp >375°; infrared spectrum showed ν_{max} 3350 (NH) and 1680 cm^{-1} (C=O). It dissolves in concentrated sulfuric acid with a violet color. Its yellow solution in pyridine becomes violet on addition of methanolic potassium hydroxide.

Anal. Calcd for $C_{28}H_{13}N_3O_8$: C, 64.74; H, 2.52; N, 8.09. Found: C, 64.89; H, 2.81; N, 7.77.

N-Methyl-3,3′-dinitro-2,2′-dianthraquinonylamine (17).—Compound **15** (2.7 g) was refluxed with methyl *p*-toluenesulfonate (6 ml) in the presence of potassium carbonate (6 g) in *o*-dichlorobenzene (200 ml) for 18 hr. The solution was filtered hot and the filtrate was evaporated to small bulk when orange-red prisms of **17** (1.7 g) separated, mp 374–375°. It dissolves in concentrated sulfuric acid with a violet color. Its orange solution in pyridine is unchanged on addition of methanolic potassium hydroxide.

Anal. Calcd for $C_{29}H_{15}N_3O_8$ (533): C, 65.29; H, 2.83; N, 7.88. Found: C, 65.14; H, 2.88; N, 7.61.

The mass spectrum had a molecular ion peak at *m/e* 533.

Dinaphtho[2,3-*b*:2′,3′-*i*]phenazine-5,9,14,18-tetrone (21).—The dinitro compound **15** (1.0 g) and stannous chloride dihydrate (10 g) were refluxed in a mixture of acetic acid (50 ml) and concentrated hydrochloric acid (30 ml) for 6 hr. The purple reaction mixture was filtered and the residue was washed well with water. The wet residue was refluxed with a solution of ferric chloride hexahydrate (20 g) in a mixture of concentrated hydrochloric acid (50 ml) and water (50 ml) for 3 hr, during which time the mixture became olive green. The crude linear indanthrone **2** was filtered off and washed well with water and sodium acetate solution, and dried in air (0.65 g). This product (0.3 g) was refluxed in acetic acid (500 ml) containing 5 drops of concentrated nitric acid for 18 hr, during which time the reaction mixture became yellow. After cooling the mixture was filtered and the residue was crystallized from *o*-nitroanisole affording fine, yellow needles of the phenazine **21** (220 mg), mp >360°; infrared spectrum showed ν_{max} 1678 cm^{-1} (C=O), with no absorption in the NH region. It dissolves in concentrated sulfuric acid with a reddish brown color.

Anal. Calcd for $C_{28}H_{12}N_2O_4$ (440): C, 76.36; H, 2.75; N, 6.36. Found: C, 76.11; H, 2.60; N, 6.41.

Its mass spectrum had a molecular ion peak at *m/e* 440.

7,16-Dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine-5,9,14,18-tetrone (Linear Indanthrone) (2).—The phenazine **21** (66 mg) was dissolved in boiling quinoline (200 ml) and hydrogen was slowly bubbled through the solution for 24 hr, during which time the solution became dark colored. The linear indanthrone (**2**) obtained after filtration and washing with quinoline, ethanol, and ether was olive green in color and consisted of fine needles (58 mg), mp >400°, very sparingly soluble in boiling quinoline: infrared spectrum, ν_{max} 3320 (NH) and 1662 cm^{-1} (C=O). It dissolves in concentrated sulfuric acid with a brownish green color, a dark green precipitate of linear indanthrone being obtained on addition of water. On warming with sodium hydrosulfite in aqueous sodium hydroxide a reddish brown solution was obtained. Exposure of this solution to air regenerated the green linear indanthrone. Addition of methanolic potassium hydroxide to a suspension of **2** in hot pyridine yields a reddish brown color.

Anal. Calcd for $C_{28}H_{14}N_2O_2$ (442): C, 76.01; H, 3.19; N, 6.33. Found: C, 75.76; H, 3.37; N, 6.59.

Its mass spectrum (inlet temperature 450°) had a molecular ion peak at *m/e* 442.

7-Methyl-7,16-dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine-5,9,14,18-tetrone (18).—On refluxing the dinitro compound **17** (1.7 g) with stannous chloride dihydrate (17 g) in a mixture of acetic

(18) K. Lagodzinski, *Ann.*, **342**, 90 (1905).

(19) R. Scholl, *Ber.*, **37**, 4427 (1904).

acid (50 ml) and concentrated hydrochloric acid (30 ml) for 12 hr, a dark violet precipitate of the diamino compound was produced. Oxidation of this compound with ferric chloride in hydrochloric acid, as described in the previous section, yielded linear N-methylindanthrone (**18**), which on crystallization from boiling quinoline was obtained as fine dark green needles, mp >375°; infrared spectrum showed ν_{max} 3320 (NH) and 1662 cm^{-1} (C=O). It dissolves in concentrated sulfuric acid with a greenish brown color. Addition of methanolic potassium hydroxide to a suspension of the substance in pyridine affords a bright red color. It yields a reddish brown vat with alkaline sodium hydrosulfite.

Anal. Calcd for $C_{29}H_{16}N_2O_4$ (456): C, 76.31; H, 3.53; N, 6.14. Found: C, 76.22; H, 3.60; N, 6.21.

The mass spectrum had a molecular ion peak at *m/e* 456, and a strong peak at 441 due to loss of CH_3.

7,16-Dimethyl-7,16-dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine-5,9,14,18-tetrone (**19**).—Linear N-methylindanthrone (**18**, 0.5 g) was refluxed with a mixture of methyl *p*-toluenesulfonate (3.5 ml) and potassium carbonate (3.5 g) in *o*-dichlorobenzene (200 ml) for 18 hr. The mixture was cooled and filtered, and the residue was washed with ethanol, water, and finally ethanol. The black residue was crystallized from quinoline (charcoal) affording dark green needles of linear N,N′-dimethylindanthrone (**19**, 150 mg), mg >375°, having no absorption in the NH region of the infrared spectrum, and a C=O absorption at 1656 cm^{-1}. It dissolves in concentrated sulfuric acid with a green color. Its green solution in hot pyridine was unchanged on addition of methanolic potassium hydroxide. It gives a reddish brown vat with alkaline sodium hydrosulfite. This dimethyl compound was also obtained by methylation of the linear indanthrone **2**, using the same experimental conditions as described for the methylation of linear N-methylindanthrone.

Anal. Calcd for $C_{30}H_{18}N_2O_4$ (470): C, 76.58; H, 3.86; N, 5.96. Found: C, 76.32; H, 3.56; N, 5.65.

Its mass spectrum had a molecular ion peak at *m/e* 470, with peaks at 455 and 440 due to loss of one and two methyls, respectively. There was a strong peak at 235, presumably due to symmetrical cleavage of the molecule into two parts.

2,3-Diaminoanthracene.—A mixture of 2,3-diaminoanthraquinone (18 g), zinc dust (12 g), and aqueous 5% sodium hydroxide (250 ml) was refluxed with stirring for 12 hr, during which time the mixture turned from deep red to yellow. The mixture was filtered hot and the residue was washed with water. The dried residue was extracted with boiling nitrobenzene (charcoal) affording 2,3-diaminoanthracene (15.2 g) as pale, greenish yellow plates, mp 270–290° dec. It dissolves in concentrated sulfuric acid with a greenish yellow color.

Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.41; H, 6.11; N, 13.65.

5(?),7,16,18(?)-Tetrahydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine (**20**).—2,3-Diaminoanthracene (3.9 g) was refluxed with stirring in a mixture of *o*-dichlorobenzene (40 ml) and acetic acid (2.5 ml) for 4 hr. During this time the pale green solution deposited a bright yellow solid (1.7 g), which crystallized from N,N-dimethylformamide as fine, yellow needles, mp above 360°; infrared spectrum showed ν_{max} 3400 cm^{-1} (NH); ultraviolet spectrum showed λ_{max} 262 mμ (log ε 4.85), 269 (4.72), 318 (3.83). It dissolves in concentrated sulfuric acid with a deep blue color.

Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Calcd for $C_{28}H_{18}N_2$: C, 87.93; H, 4.74; N, 7.33. Found: C, 87.70; H, 5.43, 5.23; N, 7.51.

Treatment with methyl *p*-toluenesulfonate in boiling *o*-dichlorobenzene in the presence of potassium carbonate afforded **7,16-dimethyl-7,16-dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine**, mp above 360°; ultraviolet spectrum showed λ_{max} 2.62 mμ (log ε 5.22), 269 (5.17), 330 (5.15). It dissolves in concentrated sulfuric acid with a deep violet-blue color. Its solutions in organic solvents have an intense green fluorescence.

Anal. Calcd for $C_{30}H_{22}N_2$ (410): C, 87.77; H, 5.40; N, 6.82. Found: C, 87.38; H, 5.68; N, 6.35.

Its mass spectrum had a molecular ion peak at *m/e* 410.

Oxidation of Compound 20.—Sodium dichromate (2.0 g) was added in small portions to a suspension of compound **20** (0.78 g) in boiling acetic acid (30 ml) during 10 min. After refluxing for an additional 30 min, the mixture was added to water. The resultant precipitate was dried and crystallized from N,N-dimethylformamide affording the phenazine **21** (0.33 g), identical with material obtained by the nitric acid oxidation of linear indanthrone **2**. Reduction of the product with hydrogen in boiling quinoline as previously described afforded the linear indanthrone.

Substituent Effects in 1,10-Phenanthrolines. I. Equilibria

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The Hammett equation has been applied to the dissociation of substituted phenanthrolinium ions, equilibrium constants for dissociation of substituted phenanthroline–iron(II) and –copper(II) complexes, and formal oxidation–reduction potentials of substituted phenanthroline–iron(II) and –copper(II) complexes. The dissociation constants of 2-, 3-, and 4-substituted phenanthrolinium ions are shown to be macroconstants related to the microconstants for protonation at N^1 and N^{10}. The 5-substituted phenanthrolines appear to undergo protonation at the oxygen atom of the hydrate. Good to excellent correlations with the extended Hammett equation were obtained in most cases. Electrical effects upon oxidation–reduction potentials of tris(5-substituted 1,10-phenanthroline)–iron(II) complexes are very much different in composition from electrical effects on dissociation of these complexes and apparently of electrical effects on dissociation of the corresponding phenanthrolinium ions. The α values obtained from the correlation of the oxidation–reduction potentials of the iron complexes are linear in the H_0 values of the solutions in which they were determined. The significant correlation of dissociation constants for 2-, 3-, and 4-substituted phenanthrolinium ions with the extended Hammett equation shows that the application of the Hammett equation to tautomeric equilibria as described by Kabachnik and co-workers will not be correct in all cases.

Substituted 1,10-phenanthrolines have long been of considerable interest as analytical reagents. A large body of data has accumulated in the literature on the ionization constants of these substances, equilibrium constants for their complex formation with transition metal ions, and oxidation–reduction potentials of the resulting complexes. We have recently studied the application of the Hammett equation[1] (1) to various heterocyclic systems.[2] It seemed of interest to extend these studies to substituent effects in 1,10-phenanthrolines. Although sporadic attempts have been made previously to apply the Hammett equation to these

$$Q_X = \rho\sigma_X + h \quad (1)$$

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