

extracted with hot benzene, leaving 2.05 g. (16.7% yield) of insoluble white solid, m.p. 170.8–173.6°. Recrystallization from acetonitrile improved the melting point only slightly (m.p. 172–174°); λ_{\max} 222–227,* 243, 248.5, 274–277,* 283, 315, 321–325, and 328 m μ . ($\epsilon = 32,300, 48,600, 52,600, 4,600, 4,790, 4,175, 3,640,$ and $5,150.$) The infrared spectrum in acetonitrile solution shows absorption at 2.85 μ and 3.05 μ attributed, respectively, to the OH and NH functions.

Anal. Calcd. for C₁₅H₁₆N₂O: C, 75.00; H, 6.66; N, 11.66; O, 6.66. Found: C, 74.46; H, 6.51; N, 11.94; O, 6.99.

The *picrate* was prepared in methanol and crystallized from methyl Cellosolve, m.p. 233.5–235.2°.

Anal. Calcd. for C₂₁H₁₉N₃O₈: C, 53.73; H, 4.05; N, 14.91; O, 27.31. Found: C, 53.93; H, 4.18; N, 15.15; O, 27.21.

8,9,10,11-Tetrahydrobenzo[e]pyrido[a]benzimidazole (V). Evaporation of the benzene extracts of the crude product IV and crystallization of the solid from benzene gave 0.98 g. (8.8% yield of white clusters, m.p. 160.2–162.2°. Recrystallization from benzene gave pure V, m.p. 161.5–162.5°.

5,6-Dihydrobenzo[e]pyrido[a]benzimidazole (VII), was prepared by Reitmann's method.⁷ Crystallization from methylcyclohexane gave short, white needles, m.p. 159.4–160.6° (lit.⁷ 157°); λ_{\max} 253, 283–288, 298, 327–333, 341, and 356 m μ . ($\epsilon = 34,200, 5210, 4560, 10,980, 12,800,$ and $8290.$)

Solution in hydrochloric acid gave the hydrochloride, which was purified by crystallization from methanol–ethyl acetate or from butanol. The fluffy white crystals had an *instantaneous* melting point of 307–308°.

Anal. Calcd. for C₁₅H₁₂N₂·HCl: C, 70.15; H, 5.06; N, 13.85; O, 10.91. Found: C, 69.96; H, 5.08; N, 13.97; O, 10.54.

The *picrate* was prepared in methanol and crystallized from methyl Cellosolve, m.p. 249–250°.

Anal. Calcd. for C₂₁H₁₈N₃O₇: C, 56.12; H, 3.34; N, 15.59; O, 24.94. Found: C, 56.05; H, 3.03; N, 15.31; O, 25.04.

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Some 9,10-Disubstituted Phenanthrenes

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For the synthesis of some new vat dye systems, a quantity of 9-bromo-10-nitrophenanthrene was required. The best procedure for the nitration of 9-bromophenanthrene to produce the 9-bromo-10-nitro compound, was described by Callow and Gulland.¹ Although the yield of pure material is only about 15%, this compound is potentially interesting as the starting point for a number of syntheses.

In an effort to prepare 10,10'-dinitro-9,9'-biphenanthryl, treatment of 9-bromo-10-nitro-

phenanthrene with copper powder in refluxing triethylbenzene gave no reaction, whereas the use of nitrobenzene as a solvent produced a black tar. The bromine atom also appeared surprisingly inert to nucleophilic displacement by several reagents. The bromonitro compound was recovered unchanged from treatment with boiling methanolic sodium methoxide or *p*-toluenesulfonamide in methyl Cellosolve, although boiling with piperidine readily gave 9-nitro-10-piperidinophenanthrene.

Several attempts were made to replace the halogen by cyanide before the proper conditions were found. Refluxing the bromonitro compound in pyridine with cuprous and potassium cyanides and a little acetonitrile afforded a fairly good yield of 10-nitro-9-phenanthrenecarbonitrile. However, the use of neither potassium cyanide in ethanol, nor cuprous cyanide in pyridine or in benzyl cyanide gave the desired reaction. When the nitrobromo compound was treated with cuprous and potassium cyanides in dimethyl sulfoxide, the sole product isolated (in 7% yield) was 9,10-phenanthrenedicarbonitrile. Presumably hydroxyphenanthrenes constituted the major products in this experiment.

Attempts to hydrolyze the nitronitrile by the action of 85% phosphoric or 96% sulfuric acids in boiling acetic acid, or by the action of hot polyphosphoric acid, left it unaffected. Under alkaline conditions, hydrolysis of the nitro group occurred, and 10-hydroxy-9-phenanthrenecarbonitrile was formed. Catalytic reduction of the nitronitrile produced 10-amino-9-phenanthrenecarbonitrile.

Reduction^{2,3} of 9-bromo-10-nitrophenanthrene with stannous chloride, zinc and acid or ammonium sulfide, was known to be accompanied by debromination to yield 9-aminophenanthrene. This is, in fact, the major evidence for the constitution of the nitrobromo compound. Reduction by means of hydrazine and a palladium catalyst^{4,5} also was accompanied by debromination. The lability of the halogen is not a specific characteristic of the 9,10-bromonitro compound, however, since an isomeric bromonitrophenanthrene (*v.i.*) and even 9-bromophenanthrene itself suffer hydrogenolysis of the bromine when treated with hydrogen in the presence of palladium. By employing a "neutral iron reduction" it was possible to isolate 10-bromo-9-phenanthrylamine in 35% yield.

Nitration of 9-acetamidophenanthrene⁶ gave, in very low yield, an acetamidonitrophenanthrene, almost certainly the 9,10-isomer.

During one run of the nitration of 9-bromophenanthrene a product isomeric with the 9,10-bromo-

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nitro compound was isolated from the mother liquors. This 9-bromo-x-nitrophenanthrene (m.p. 190.0–198.8°) was converted by the von Braun reaction into the 9-cyano-x-nitro homolog (m.p. 265.0–267.5°). Despite the proximity of these melting points to those of the 9,10-isomers, mixture melting points showed in each case a significant depression, and the infrared spectra of the two sets of isomers were clearly different. Reduction by means of hydrazine and palladium-charcoal readily gave a phenanthrylamine identified as the 3-isomer. This evidence establishes the nitrobromo compound as the 3,9- or 3,10-derivative. A choice between these structures cannot be made with certainty from the evidence at hand, although, inasmuch as acetylation of 9-bromophenanthrene has been shown⁷ to yield the 3-acetyl-9-bromo compound, it seems probable that our product is 9-bromo-3-nitrophenanthrene.

EXPERIMENTAL⁸

9-Bromo-10-nitrophenanthrene was prepared by Callow and Gulland's procedure.¹ Crystallization of the crude reaction product three times from benzene gave yellow needles of pure material, m.p. 209.5–211.0° (lit. m.p. 207–208°⁹ or 195–203°¹) in 12–15% yield.

10-Nitro-9-piperidinophenanthrene. A mixture of 3.02 g. of nitrobromophenanthrene, 6.0 ml. of piperidine, and a trace of cuprous chloride was boiled under reflux for an hour, then diluted with water. The resulting oil solidified when triturated with water, and the solid was crystallized three times from methanol giving 1.40 g. (46% yield) of golden yellow platelets, m.p. 136.4–137.2°.

Anal. Calcd. for $C_{15}H_{13}N_2O_2$: C, 74.51; H, 5.88; N, 9.15. Found: C, 74.40; H, 5.94; N, 9.21.

10-Nitro-9-phenanthrenecarbonitrile. A mixture of 3.00 g. of bromonitrophenanthrene, 2.00 g. of potassium cyanide, 2.00 g. of cuprous cyanide, 2.0 ml. of acetonitrile, and 10.0 ml. of dry pyridine was stirred and boiled under reflux for 16.5 hr. The dark reaction mixture was poured into water and the solid was filtered, washed with water, and dried. Extraction with boiling toluene, and concentration of the extracts yielded yellow crystals, m.p. 259–265°. Recrystallization from benzene gave 1.30 g. of yellow needles, m.p. 265.0–267.7°.

Anal. Calcd. for $C_{15}H_9N_2O_2$: C, 72.62; H, 3.23; N, 11.29. Found: C, 72.60; H, 3.19; N, 11.00.

9,10-Phenanthrenedicarbonitrile. The preceding experiment was duplicated with the exception that the 10 ml. of pyridine was replaced by 20 ml. of dimethyl sulfoxide. A dull yellow solid (0.32 g., m.p. 283–287°) was the sole product isolated. Two crystallizations from chlorobenzene (charcoal) afforded 0.20 g. of yellow needles, m.p. 290–292°. The infrared spectrum was extremely simple and showed a nitrile absorption at 4.50μ .

Anal. Calcd. for $C_{16}H_8N_2$: C, 84.21; H, 3.51; N, 12.28. Found: C, 84.40; H, 3.75; N, 12.10.

9-Amino-10-phenanthrenecarbonitrile. Hydrogenation of 2.48 g. of 9-nitro-10-phenanthrenecarbonitrile and 0.70 g. of 10% palladium-charcoal in 50 ml. of ethanol, followed by crystallization of the product from ethanol, gave a pale

yellow solid m.p. 173.6–178.0°. Two recrystallizations from benzene removed an insoluble fraction and afforded 0.85 g. of nearly white, felted needles having an instantaneous melting point of 176–177°. If put into the bath below 175°, the compound decomposes over a range.

Anal. Calcd. for $C_{15}H_{10}N_2$: C, 82.57; H, 4.59; N, 12.84. Found: C, 82.50; H, 4.58; N, 13.20.

9-Hydroxy-10-phenanthrenecarbonitrile. A solution of 2.48 g. of 9-nitro-10-phenanthrenecarbonitrile and 2.50 g. of potassium hydroxide in 2 ml. of water and 12 ml. of methyl Cellosolve was boiled under reflux for 0.5 hr., then diluted with 125 ml. of water. Acetic acid was added to bring the pH to near neutrality, and the milky solution was treated with charcoal and filtered. Acidification of the filtrate yielded 1.83 g. (83.5%) of pale greenish solid. Crystallization from acetic acid (charcoal) gave 1.00 g. of yellow solid, m.p. 242–244°. Two recrystallizations from toluene and one from glycol diacetate afforded 0.40 g. of pale yellow needles, m.p. 247–249°. The infrared spectrum showed the expected bands at 3.15 and 4.50μ arising from the OH and CN functions.

Anal. Calcd. for $C_{15}H_9NO$: C, 82.19; H, 4.10; N, 6.40; O, 7.30. Found: C, 82.22; H, 3.83; N, 6.22; O, 7.38.

The benzoate ester, after three crystallizations from toluene, formed white prisms, which, when immersed in the heating bath at 195°, sweat and partially melt at 202–204°, then resolidify and melt at 209.0–209.5°.

Anal. Calcd. for $C_{21}H_{15}NO_2$: C, 80.51; H, 4.79; N, 4.47. Found: C, 80.50; H, 4.50; N, 4.65.

10-Bromo-9-phenanthrylamine. A mixture of 5.0 g. of fine iron filings, 10 ml. of water, and 1 ml. of acetic acid was stirred and boiled under reflux for 20 min. Then 3.02 g. of bromonitrophenanthrene and 10 ml. of ethanol were added, and the boiling was continued overnight. The thick reaction mixture was extracted three times with 40-ml. portions of boiling benzene. The combined, dried benzene extracts were treated with hydrogen chloride and the precipitated amine hydrochloride (3.15 g.) was filtered, washed with benzene, and dried. The salt was dissolved in pyridine and poured into water, and the free amine was filtered and dried (wt. 2.38 g.). Two crystallizations from cyclohexane gave very fine white needles, m.p. 131.0–131.7° (dec.).

Anal. Calcd. for $C_{14}H_{10}BrN$: C, 61.76; H, 3.68; Br, 29.40; N, 5.15. Found: C, 62.13; H, 3.81; Br, 29.12; N, 5.20.

9-Acetamido-10-nitrophenanthrene. To a solution of 0.50 g. of 9-acetamidophenanthrene in 40 ml. of acetic acid, was added 1.30 ml. of a 10% solution of nitric acid (d. 1.4) in acetic acid. The solution was warmed on a steam bath for 2 hr., then was diluted with water and filtered. The resulting brown solid (0.45 g.) was crystallized twice from ethyl acetate, giving 50 mg. of light yellow product, m.p. 267.5–269.0°.

Anal. Calcd. for $C_{16}H_{12}N_2O_3$: C, 68.57; H, 4.29; N, 10.00. Found: C, 68.30; H, 4.83; N, 9.90.

9-Bromo-3(or 6?)-nitrophenanthrene. Concentration of the mother liquors from one run of the preparation of 9-bromo-10-nitrophenanthrene yielded a small crop of crystalline solid, which upon recrystallization from benzene, gave yellow needles, m.p. 190.0–191.8°.

Anal. Calcd. for $C_{14}H_8BrNO_2$: C, 55.62; H, 2.65; Br, 26.5; N, 4.64; O, 10.60. Found: C, 55.70; H, 2.81; Br, 26.3; N, 4.31; O, 10.00.

3(or 6?)-Nitro-9-phenanthrenecarbonitrile. In the same manner employed for the 9,10-isomer, 1.00 g. of 9-bromo-3-nitrophenanthrene was subjected to the von Braun reaction. Four crystallizations from acetic acid yielded 0.20 g. of pale yellow microneedles, m.p. 268–269°.

Anal. Calcd. for $C_{15}H_9N_2O_2$: C, 72.62; H, 3.23; N, 11.29; O, 12.90. Found: C, 72.39; H, 3.03; N, 11.47; O, 13.07.

3-Phenanthrylamine. A slurry of 50 mg. of 9-bromo-3-nitrophenanthrene, 20 mg. of 10% palladium charcoal, 0.50 ml. of 85% hydrazine hydrate, and 5 ml. of ethanol was stirred and boiled for 5 min. The catalyst was filtered off and the filtrate was evaporated. The solid was washed with water and crystallized from methyl cyclohexane, giving 28

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mg. (87.5% yield) of white leaves, m.p. 83.5–86.0° (lit.⁵ 86–87°). Treatment with acetic anhydride and pyridine gave 3-acetamidophenanthrene, m.p. 202.5–203.5° (lit.¹⁰ 200–201°).

9-Phenanthrylamine was obtained from 9-bromo-10-nitrophenanthrene (in 91% yield) in a manner analogous to the preparation of the 3-isomer. It crystallized in white felted needles, m.p. 136.8–137.8° (lit.¹¹ 136–137.5°). The acetyl derivative formed white needles, m.p. 214.5–215.0° (lit.⁶ 213–215°).

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Preparation and Molecular Complexes of Tetrahalophthalate Esters

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The molecular complexing properties of tetrahalophthalic anhydrides have been the subject of several studies,^{1–5} but the molecular complexing properties of the tetrahalophthalate esters have not been investigated, although the yellowish green color of a dimethyl tetrachlorophthalate-dimethylaniline mixture has been reported.² This report on some of the complexing properties and synthesis of several tetrahalophthalates, two of which have not previously been characterized, resulted from finding that these materials were useful gas chromatographic liquid phases for aromatic materials.⁶ Separation and retention on gas chromatographic columns containing the tetrahalophthalates is a function of the electron donor characteristics of the aromatic hydrocarbons. Details will be reported elsewhere.

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The molecular complexing behavior of the tetrahalophthalates reported here and their low melting points suggest that they may be useful reagents for separation and/or purification of the polyalkylaromatic fractions from coal tar and petroleum. Conversely, interaction with an aromatic hydrocarbon could be used for purifying and separating the tetrahalophthalate esters themselves.

Data on the tetrahalophthalate esters that were prepared are listed in Table I. Where possible, we prefer a modification of the azeotropic distillation procedure of Nordlander and Cass⁷ for preparation of the symmetrical diesters. The reaction of the potassium salt of the monoalkyl ester and the alkyl halide⁸ was used for preparation of the mixed ester.

Solid hexamethylbenzene 1:1 complexes of di-*n*-propyl tetrachlorophthalate, di-*n*-butyl tetrachlorophthalate, and di-*n*-propyl tetrabromophthalate were isolated from solution. All were white crystalline solids. The intensity of yellow color on initial mixing of the chlorophthalates with hexamethylbenzene was in the order di-*n*-butyl > di-*n*-propyl. Methyl propyl tetrachlorophthalate did not give a solid complex with hexamethylbenzene by our procedure; mixtures of these two materials gave only a faint yellow color even in concentrated solution.

The light yellow colors observed on mixing the tetrachlorophthalates with durene, isodurene, and hemimellitene probably indicate complex formation. Evidently interaction with mesitylene (no color) is weaker; this may be due to a steric factor.⁹

The interactions of the tetrahalophthalates with dimethylaniline are also of interest. The colors of the solutions obtained undoubtedly indicate complex formation and suggest the possible use of tetrahalophthalates as liquid substrates for aromatic amines in gas chromatography.

EXPERIMENTAL

*A. Di-*n*-propyl tetrachlorophthalate.* A mixture of 288 grams (1.01 mole) of tetrachlorophthalic anhydride, 360 grams (6 moles) of propyl alcohol, 4 grams (0.021 mole) of *p*-toluenesulfonic acid monohydrate, and 35 ml. of benzene was refluxed continuously for 16 days in a flask, fitted with a 6-in. Vigreux column connected to a Dean-Stark trap and condenser. With slow reflux, a total of 25.5 ml. of aqueous phase separated in the trap. At intervals, additional *p*-toluenesulfonic acid (3 × 1 g.) and small aliquots of benzene were added.

Volatile material was distilled from the flask up to a pot temperature of 168°. The cooled residue was extracted with 6% aqueous sodium bicarbonate which was then extracted with benzene.

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