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Tetraanthraquinonoporphyrazines: I. Substituted 2,3-Dicarboxyanthraquionones

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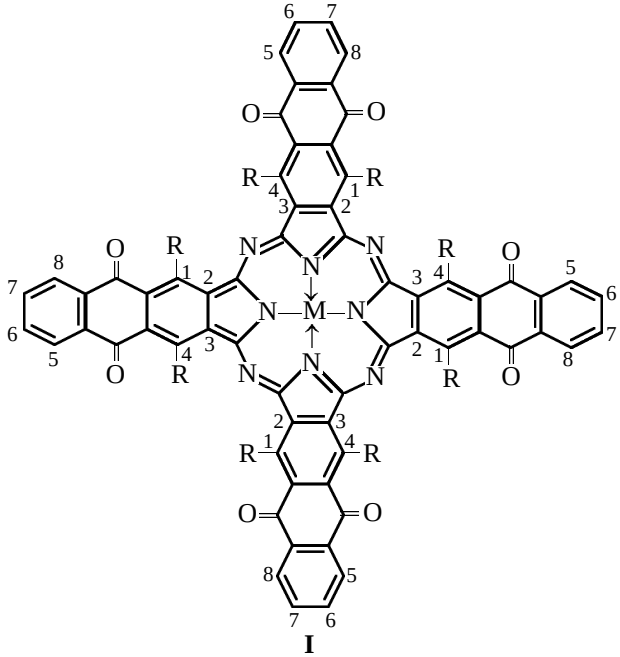
Abstract — New procedures were developed for preparing substituted 2,3-dicarboxyanthraquinones by acylation of arenes with pyromellitic anhydride, followed by intramolecular cyclization of the products. The 2,3-dicarboxyanthraquinones prepared were further modified by oxidation, sulfonation, nitration, and reduction.

One of the routes of chemical modification of the phthalocyanine molecule is annelation at the benzene rings with the formation of various porphyrazines, structural analogs of phthalocyanine. Although numerous compounds of this class have been prepared [1–6], complexes containing naphthoquinone rings, tetraanthraquinonoporphyrazines, remain poorly studied. Published data on these compounds mainly concern metal complexes of unsubstituted (**I**, R = H, M = VO, Fe, Co, Zn) [7–10] and 1,4-substituted (**I**, R = NH_2, OCH_3, OH, Cl, CH_3; M = Fe, Co, Ni, Mn, Cr, Zn) tetraanthraquinonoporphyrazines [11–15].



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It should be noted that the most studied are the properties of octa-1,4-hydroxytetraanthraquinonoporphyrazines (tetraquinizarinoporphyrazines) [11–14], whereas the properties of other derivatives [13] are virtually unknown. Data on the synthesis and properties of porphyrazines substituted at other positions of the anthraquinones fragments are scarce [15], although these compounds are of certain interest. We believe that the main factor impeding their study is the lack of starting compounds for their synthesis.

To fill this gap, we made this study aimed to develop procedures for preparing 2,3-dicarboxyanthraquinone and its 5- and 6-substituted derivatives, which

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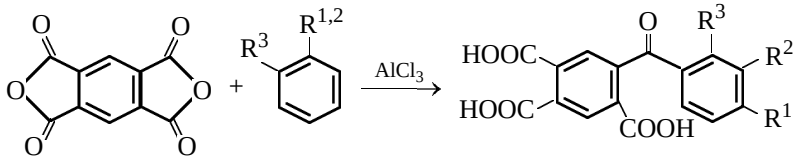
can be used as starting compounds for preparing the corresponding tetraanthaquinonoporphyrazines.

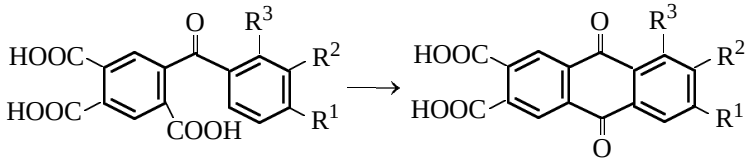
Data are available on preparation of *o*-dicarboxylic acids derived from anthraquinone by acylation of *o*-xylene with phthalic anhydride [8] and of di- or trimethyl-substituted benzenes with aroyl chlorides [16, 17], followed by intramolecular cyclization and oxidation of the resulting compounds. We have developed procedures for preparing benzoyltrimellitic acids by acylation of arenes of various structures with pyromellitic dianhydride in the presence of $AlCl_3$:

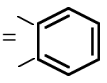


R^1 = H, Cl, CH_3; R^2 = R^3 = H; R^2 =  , R^1 = R^3 = H; R^1 = H; $R^{2,3}$ =  .

The acylation was performed in the presence of a large excess of the arene (more than 10 mol per mole of anhydride); the reaction mixture was slowly heated from 20°C to the boiling point. In the reactions with biphenyl and naphthalene, we used as the reaction medium heptane, which is inert under these conditions and imparts sufficient mobility to the reaction mixture. It should be noted that acylation yields, along with the desired product (benzoyl-substituted trimellitic acids), also the corresponding 1,3-dibenzoylbenzene-4,6-dicarboxylic acids. The separation of the product mixtures is difficult and was not performed in this study. Benzoyltrimellitic acids containing an impurity of the corresponding 1,3-dibenzoylbenzene-4,6-dicarboxylic acids were isolated by treatment of the reaction mixture with a hot 10% sodium carbonate solution, followed by acidification of the alkaline solution to pH 3–4 and filtration to isolate the precipitate. Acylation of toluene and chlorobenzene occurs at the p-position relative to the substituent, but biphenyl is acylated at the *m*-position relative to the phenyl group, because at the *o*- and *p*-positions the electron density on the C atoms is appreciably decreased relative to unsubstituted benzene [16].

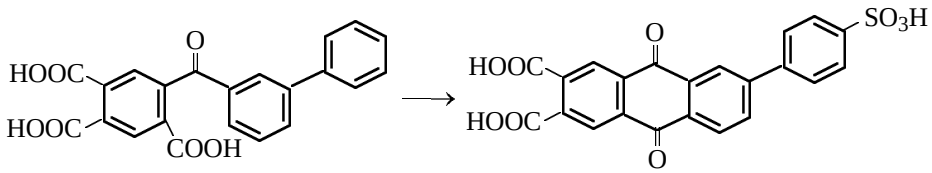
The benzoyltrimellitic acids were converted into the corresponding 2,3-dicarboxyanthraquinones by treatment with sulfuric acid monohydrate or oleum.



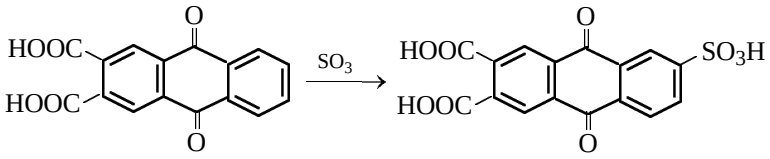
R^1 = H, R^2 = R^3 =  ; R^2 = R^3 = H; R^1 = H, Cl, CH_3.

In so doing, we must take into account the possibility of intramolecular cyclization of 1,3-dibenzoylbenzene-4,6-dicarboxylic acid impurities into the corresponding diquinones, which should be insoluble in aqueous alkaline solutions. Therefore, isolation and purification of 2,3-dicarboxyanthraquinone and its substituted derivatives was performed by repeated dissolution of the reaction products in an aqueous alkaline solution, followed by precipitation of the desired compounds by acidification of the filtrate.

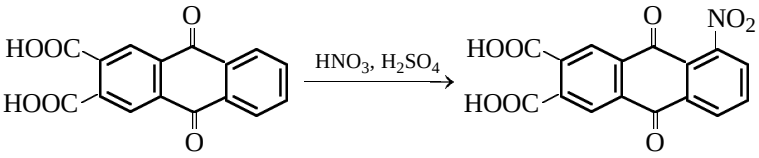
It is known that intramolecular cyclization of *o*-(*m*-phenyl)benzoylbenzoic acid is accompanied by sulfonation of the phenyl moiety at the *p*-position [16]. Thus, by intramolecular cyclization of 5-(*m*-phenylbenzoyl)trimellitic acid we obtained 2,3-dicarboxy-6-(*p*-sulfophenyl)anthraquinone.



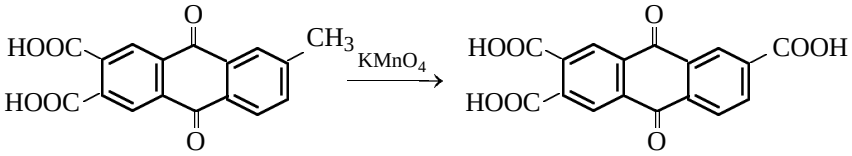
The presence of electron-withdrawing substituents in the arene being acylated prevents formation of *o*-benzoylbenzoic acids [16]; therefore, the sulfo and nitro groups were introduced directly into the 2,3-dicarboxyanthraquinone prepared beforehand. In particular, 2,3-dicarboxy-6-sulfoanthraquinone was prepared by sulfonation of 2,3-dicarboxyanthraquinone with 25% oleum:



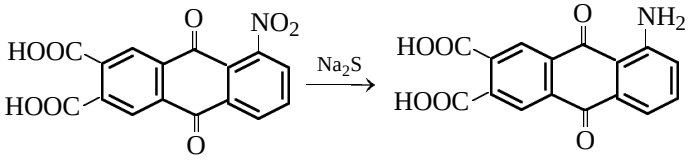
2,3-Dicarboxy-5-nitroanthraquinone was prepared by nitration of 2,3-dicarboxyanthraquinone under the conditions given in [18] for 1-nitroanthraquinone:



Farberov *et al*. [17] prepared 2,3,6-tricarboxyanthraquinone by acylation of pseudocumene with p-toluyl chloride, followed by oxidation of the intermediate with nitric acid and by intramolecular cyclization with oleum. We prepared this compound by oxidation of 2,3-dicarboxy-6-methylanthraquinone. The characteristics of the resulting product were fully consistent with published data [17].



5-Amino-2,3-dicarboxyanthraquinone was prepared by reduction of 5-nitro-2,3-dicarboxyanthraquinone under the conditions given in [18] for 5-nitroanthraquinone.



A characteristic feature of the IR spectra of 2,3-dicarboxyanthraquinone and its substituted derivatives is a strong band in the range 1700–1710 cm^{-1}, corresponding to carboxy groups [19] and absent in the spectrum of the unsubstituted anthraquinone.

The compositions of 2,3-dicarboxyanthraquinone and its derivatives were confirmed by elemental analysis.

The presence of functional substituents (SO_3H and Cl) in the 2,3-dicarboxyanthraquinone molecule is also confirmed by chemical transformations. Qualitative reactions with $BaCl_2$ and $AgNO_3$ revealed the presence of SO_4^{2-} and Cl^- ions, respectively, in the solutions after the breakdown of 2,3-dicarboxy-6-sulfo-, 2,3-dicarboxy-6-(*p*-sulfophenyl), and 2,3-dicarboxy-6-chloroanthraquinone with concentrated nitric acid. The presence of the amino group in 5-amino-2,3-dicarboxyanthraquinone was confirmed by diazotization followed by coupling with a P-salt solution to obtain a colored compound.

Our preliminary attemts to obtain from the synthesized compounds substituted tetraanthraquinonoporphyrazines by template synthesis were successful; their results will be reported in a separate paper.

EXPERIMENTAL

Acylation of benzene, chlorobenzene, and toluene *(general procedure).* A 15.3-g portion of anhydrous $AlCl_3$ was added with vigorous stirring to 10.0 g of pyromellitic dianhydride and 25 ml of benzene or its derivative. After stirring for 2 h, the mixture was gradually heated on a water bath to 75–80°C over a period of 4 h and kept at this temperature for 10 h. After cooling, 50 ml of water was added, and the mixture was allowed to stand for 30 min. The resulting suspension was treated with an excess of a hot 10% solution of sodium carbonate. The precipitate of aluminum hydroxide was filtered off. The aqueous and organic phases of the filtrate were separated. The aqueous layer was acidified with HCl to pH 3–4 and allowed to stand for 5 h at 10–15°C. The precipitate thus formed was filtered off, washed with water to neutral reaction, and dried at 80–90°C.

Acylation of biphenyl. A 10.0-g portion of pyromellitic dianhydride was mixed with 13.0 g of biphenyl and 20 ml of heptane. The mixture was heated to 50°C, and 15.3 g of anhydrous $AlCl_3$ was added with stirring. The mixture was refluxed (~100°C) for 3 h, after which the heptane was distilled off, and the mixture was heated for an additional 6 h at 120–130°C. After cooling, 50 ml of water and 10 ml of concentrated HCl were added; the mixture was stirred for 12 h. The precipitate thus formed was filtered off, washed with hot water, and boiled for 30–40 min in a 10% sodium carbonate solution. The solution was filtered while hot, and the precipitate was treated as described above 3–4 times more. The filtrates were combined, acidified with HCl to pH 3–4, and allowed to stand for 5 h at 10–15°C. The precipitate thus formed was filtered off, washed with water to neutral reaction, and dried at 80–90°C.

Acylation of naphthalene was performed similarly to the acylation of biphenyl, with 10.8 g of naphthalene used instead of biphenyl.

2,3-Dicarboxyanthraquinone and its substituted derivatives *(general procedure).* A 20.0-ml portion of sulfuric acid monohydrate (in the case of the chlorine-substituted acylation product, of 16% oleum) was heated to 130°C, and 5.0 g of appropriate acylation product was added over a period of 15 min with vigorous stirring. Then the mixture was heated to 150°C and kept at this temperature for 5 h. After cooling, the mixture was poured with stirring into 200 ml of water. The precipitate thus formed was filtered off, washed with water to neutral reaction, and dissolved in a sodium carbonate solution. After acidification with HCl, a precipitate formed, which was filtered off and washed with water until the absence of chloride ions in the filtrate. The dissolution–precipitation cycle was repeated two times, and the product was dried at 80–90°C.

2,3-Dicarboxyanthraquinone. Colorless powder soluble in chloroform, DMF, aqueous sodium carbonate solution, and hot water. Yield 3.9 g (51%), mp 282°C. Found, %: C 56.7; H 2.2; Cl 10.5. $C_{16}H_7ClO_6$. Calculated, %: C 58.1; H 2.1; Cl 10.7.

2,3-Dicarboxy-6-methylanthraquinone. Colorless powder soluble in chloroform, DMF, aqueous sodium carbonate solution, and hot water. Yield 2.8 g (41%), mp 356°C. Found, %: C 64.7; H 3.4. $C_{17}H_{10}O_6$. Calculated, %: C 65.8; H 3.3.

2,3-Dicarboxybenzo[α]anthraquinone. Light yellow needles, soluble in chloroform, DMF, aqueous sodium carbonate solution, and hot water. Yield 3.5 g (27%), mp 365°C. Found, %: C 68.1; H 3.0. $C_{20}H_{10}O_6$. Calculated, %: C 69.4; H 2.9.

2,3-Dicarboxy-6-(*p*-sulfophenyl)anthraquinone. A 10-ml portion of sulfuric acid monohydrate was heated to 130°C. Then 5.0 g of the biphenyl acylation product was added over a period of 15 min with vigorous stirring, and the mixture was heated to 150°C and kept at this temperature for 5 h. After cooling, the mixture was poured with stirring into 200 ml of water, and the precipitate thus formed was filtered off. The desired product was isolated and purified by the

above-described general procedure. The product is a colorless powder soluble in chloroform, DMF, acetone, aqueous sodium carbonate solution, and hot water. Yield 6.9 g (81%), mp 267°C. Found, %: C 57.6; H 2.8; S 6.9. $C_{22}H_{12}O_9S$. Calculated, %: C 58.4; H 2.7; S 7.1.

2,3-Dicarboxy-5-nitroanthraquinone. A 9.0-g portion of 2,3-dicarboxyanthraquinone was added with stirring to 92.5 ml of sulfuric acid monohydrate. The mixture was heated to 130–140°C and stirred until the 2,3-dicarboxyanthraquinone fully dissolved (2–3 h). The solution was cooled to 50°C, and a nitrating mixture consisting of 13.5 ml of concentrated nitric acid (ρ 1.4) and 11.7 ml of 98% sulfuric acid was added dropwise over a period of 30–40 min. In so doing, the temperature rose to 80°C, and within a certain period 2,3-dicarboxy-5-nitroanthraquinone started to precipitate. The mixture was heated to 120–130°C, kept at this temperature for 2 h, and cooled; the precipitate was filtered off and washed with cold water to neutral reaction. The target product was purified similarly to the above-described general procedure. The product is a yellow powder soluble in chloroform, DMF, aqueous sodium carbonate solution, and hot water. Yield 7.2 g (69%), mp 292–294°C. Found, %: C 55.3; H 2.2; N 4.0. $C_{16}H_7NO_8$. Calculated, %: C 56.3; H 2.1; N 4.1.

2,3,6-Tricarboxyanthraquinone. Potassium hydroxide was added to 2.0 g of 2,3-dicarboxy-6-methylanthraquinone in 80 ml of water to obtain a weakly alkaline solution. The solution was heated to 90–95°C, and 3.0 g of $KMnO_4$ was added with stiring in 0.5-g portions. Each subsequent portion was added after decolorization of the previous portion (30–40 min). The resulting suspension was filtered while hot. The MnO_2 precipitate was washed with hot water. The filtrate was acidified with HCl to pH 3–4; the precipitate thus formed was filtered off and washed with ice-cold water to neutral reaction. The desired product was purified by the above-described general procedure. The product is a colorless powder soluble in chloroform, DMF, acetone, aqueous sodium carbonate solution, and water. Yield 1.4 g (62%), mp 341°C. Found, %: C 59.7; H 2.5. $C_{17}H_8O_8$. Calculated, %: C 60.0; H 2.4.

2,3-Dicarboxy-6-sulfoanthraquinone. A 16-ml portion of 20% oleum was heated to 120–140°C; 2.2 g of 2,3-dicarboxyanthraquinone was added, and the mixture was kept at this temperature for 6 h, cooled, and poured onto ice. The precipitate thus formed was filtered off, washed with 5% HCl, and dried at 80–90°C. The product is a colorless powder soluble in chloroform, DMF, aqueous sodium carbonate solution, and water. Yield 1.5 g (50%), mp 273°C. Found, %: C 50.5; H 2.2; S 8.2. $C_{16}H_8O_9S$. Calculated, %: C 51.1; H 2.1; S 8.5.

2,3-Dicarboxy-5-aminoanthraquinone. A mixture of 25 ml of water and 2 g of 2,3-dicarboxy-5-nitroanthraquinone was heated to 80°C, after which 5 g of Na_2S was added over a period of 15 min, the temperature was raised to 95°C, and the mixture was kept at this temperature for 3 h. Then the mixture was cooled, and the precipitate was filtered off, washed with ice-cold water to neutral reaction, and dried at 80–90°C. The product is a yellow powder soluble in DMF, benzene, acetone, concentrated HCl, aqueous sodium carbonate solution, and hot water. Yield 1.6 g (87%), mp 287°C. Found, %: C 61.0; H 3.0; N 4.6. $C_{16}H_9NO_6$. Calculated, %: C 61.7; H 2.9; N 4.5.

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