

Preparation and Purification of Some Oxidation Products of Perylene

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Reliable procedures are given for the purification of perylene, and for the preparation and purification of 3,10-perylenequinone, 1,12-perylenequinone, 2,11-dihydroxy-3,10-perylenequinone, 4,9-dihydroxy-3,10-perylenequinone, 4-oxo-4*H*-benz[*de*]anthracene-7,8-dicarboxylic anhydride, phenanthrene-1,8,9,10-tetracarboxylic dianhydride, and anthraquinone-1,5-dicarboxylic acid. Data on the physical properties of 3,9-perylenequinone are also reported.

Key Words: Absorption spectra, air pollutants, anthraquinone-1,5-dicarboxylic acid, dihydroxy-perylenequinones, infrared, 4-oxy-4*H*-benz[*de*]anthracene-7,8-dicarboxylic anhydride, perylene, perylenequinones, photo-oxidation products of perylene, polycyclic aromatic hydrocarbons, thin-layer chromatograms, ultraviolet, visible absorption spectra.

1. Purpose and Scope of the Project

Pure reference compounds derived from perylene, particularly various oxidation products, were needed in connection with a study of the products resulting from photochemical reactions of perylene adsorbed on various particulates. Because these compounds were not available in a suitable state of purity, the methods reported in the experimental part were developed for their synthesis and purification. Reliable procedures are given for the purification of perylene (1), and for the preparation and purification of 3,10-perylenequinone (2), 1,12-perylenequinone (3), 2,11-dihydroxy-3,10-perylenequinone (4), 4,9-dihydroxy-3,10-perylenequinone (5), 4-oxo-4*H*-benz[*de*]anthracene-7,8-dicarboxylic anhydride (6), phenanthrene-1,8,9,10-tetracarboxylic dianhydride (7), and anthraquinone-1,5-dicarboxylic acid (8). The preparation of 3,9-perylenequinone (9) is also reported.

The purification of the compounds was followed by thin-layer chromatography until constant, reproducible R_f values were obtained. For identification purposes, the infrared absorption spectra of compounds 1 to 8 were recorded; these are reproduced in figure 1. The peaks in the ultraviolet and visible spectra of these compounds are given in table 1.

2. Purification of Perylene (1)

A solution of 300 mg (0.0012 mole) of perylene (commercial grade) in 1:1 (v/v) benzene–toluene (50 ml) was introduced onto a column (3.5 × 50 cm) of silica gel (100–200 mesh), and the column was eluted with 3:1 (v/v) glacial acetic acid–benzene. A small, fore-running zone was discarded; a major yellow zone, which sometimes had a grayish purple shade, was collected and concentrated to dryness. Recrystallization from glacial acetic acid, and then from xylene, yielded lustrous yellow-orange plates; yield 250 mg (83%), mp 275 to 277 °C. A sample sublimed at 200 °C/0.05 mm had mp 276 to 278 °C; lit. mp 264 to 265 °C [1],¹ 273 to 274 °C [2].

A thin-layer chromatogram (5 × 20 cm glass plate covered with freshly activated Silica Gel G,² 250 μm thick), showed a homogeneous yellow spot that had a blue fluorescence; 2:1:1 (v/v) heptane–toluene–acetic acid (solvent A), 60 min, gave R_f 0.88 ± 0.01; 18:1:1 (v/v) heptane–toluene–acetic acid, 60 min, gave R_f 0.46 ± 0.01. If the chromatogram is spotted with a concentrated solution of perylene, two fluorescent areas are usually observed, namely, a yellow spot surrounded by a bluish halo. A thin-layer chromatogram of the purified material was in reasonable agreement with that of a sample of perylene purified by zone-refining.

If the chromatogram is exposed to iodine vapor for 2 min, the color of the spot, originally yellow, turns

¹ Figures in brackets indicate the literature references at the end of this paper.

² Certain commercial products and instruments are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products or equipment identified are necessarily the best available for the purpose.

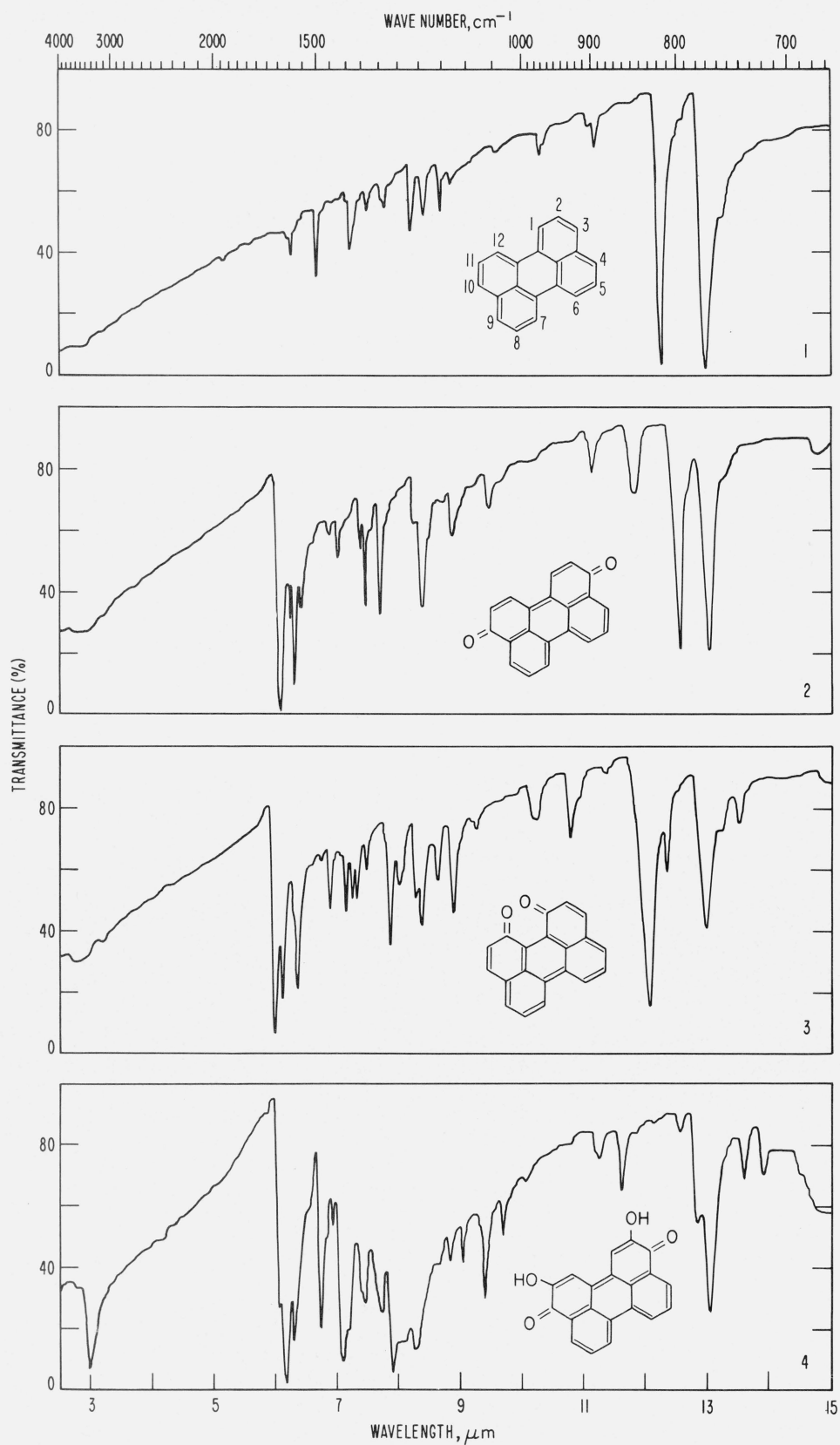


FIGURE 1. Spectrograms of compounds in potassium chloride pellets.
 1, Perylene; 2, 3,10-perylenequinone; 3, 1,12-perylenequinone; 4, 2,11-dihydroxy-3,10-perylenequinone.

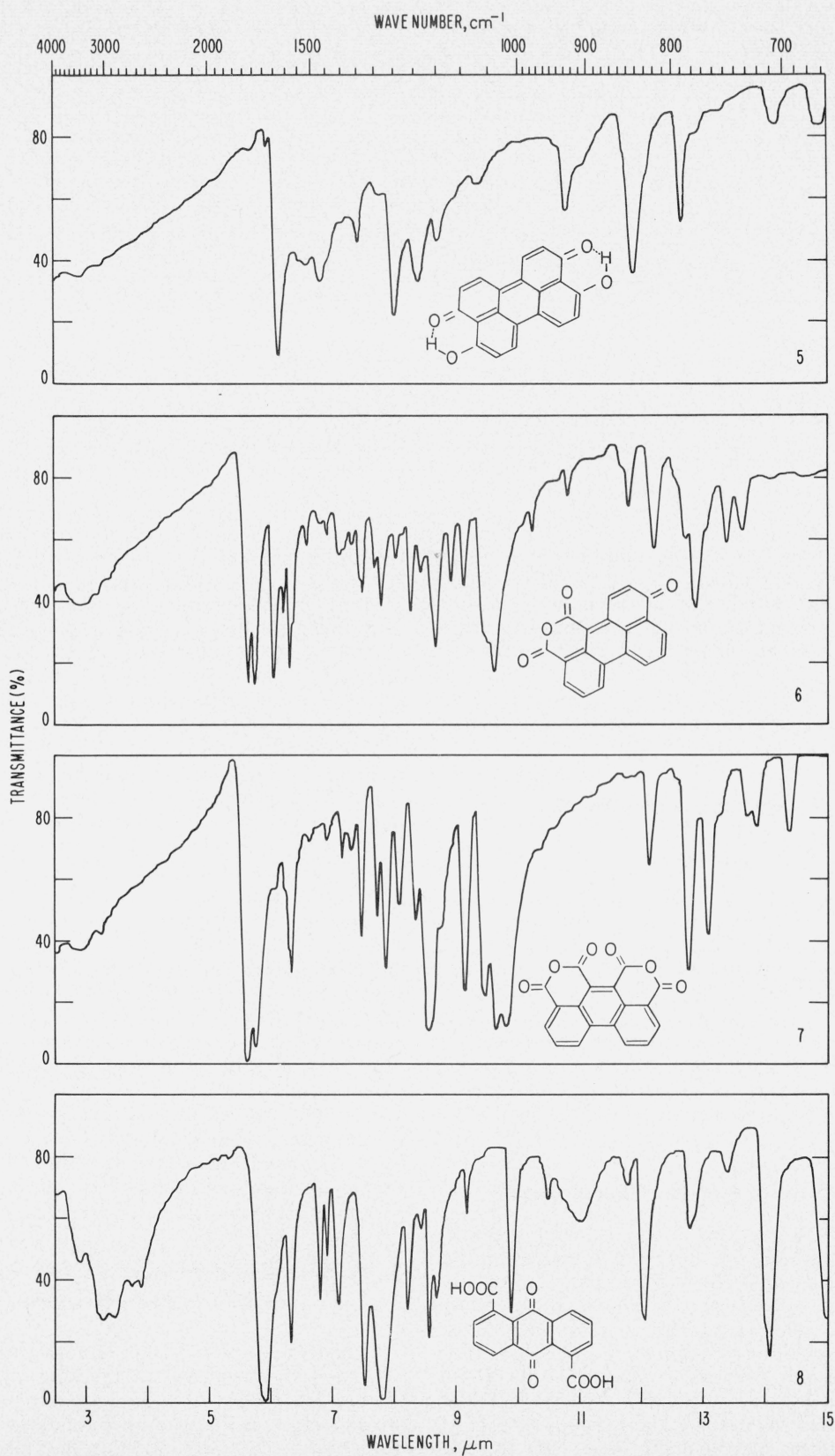


FIGURE 1. Spectrograms of compounds in potassium chloride pellets.—Continued

5, 4,9-dihydroxy-3,10-perylenequinone; 6, 4-oxo-4H-benz[de]anthracenedicarboxylic anhydride; 7, phenanthrene-1,8,9,10-tetracarboxylic dianhydride; 8, anthraquinone-1,5-dicarboxylic acid.

TABLE 1. Peaks (nm) in ultraviolet and visible spectra^a of compounds 1-9

1	2			3	4	5	6			7	8	9
	A	B	B[5]				A	B	B[5]			
225	238	241		222	222.5				215	228		
244.5	245(sh)	246(sh)		240	233		238	230(sh)	230	242		246
266	258							246.5			250	
269(sh)	266	265(sh)			253(sh)	250	256.5	254(sh)		251(sh)		
	272(sh)		271	279(sh)		279(sh)		270(sh)	287-283		272(sh)	277
	293(sh)	285	285	293(sh)			297(sh)	290	290			
	307			308(sh)				307		302		
	319	314	315	320				312(sh)	311	313	328	
	335	334(sh)					325	335				
		343(sh)	347					341				
364(sh)	350	352	354					352				
384	392(sh)	362	362						363		390	368(sh)
405	411		389									
	415(sh)			458		452	403	412(sh)		403		429
						480	422(sh)	432				
						532	488	485(sh)	470			
		548	569									527
		580	580		580	575						568

^a Key to solvents: A, absolute methanol; B, concentrated sulfuric acid; C, chloroform.

olive-brown, and the strong blue fluorescence disappears; this change is probably due to the formation of a charge-transfer complex [3] between perylene and iodine, because, when the spot is reexposed to air, it reacquires its original yellow color and blue fluorescence. This technique is useful in distinguishing between a polycyclic, aromatic hydrocarbon that forms such a complex with iodine vapor and its halogen derivatives (which usually do not).

3. 3,10-Perylenequinone (2)

3.1. Discussion

3,10-Perylenequinone (2) may be prepared by oxidation of perylene with chromic acid according to the method of Zinke and Unterkreuter [4]. Dione 2 is rather difficult to purify by recrystallization. In table 1, the ultraviolet and visible spectra of dione 2 as reported by Brown and Todd [5] are compared with those of the product purified as described in section 3.2.

Analytically pure dione 2 has been obtained by two methods of purification: (a) column chromatography on silica gel, and (b) adsorption chromatography on activated carbon.

3.2. Preparation of 3,10-Perylenequinone (2)

One gram (0.004 mole) of perylene (reagent grade) was oxidized with chromic acid (10 g of chromium trioxide in 100 ml of water) for 6 hr at 100 °C with continuous agitation, according to a published procedure [4]. The mixture was filtered while hot, and the filtrate was saved for isolation of compound 8. The crude product was washed with water, and dried at 50 °C; yellowish brown powder, yield 1.0-1.05 g (89-94%).

Crude 3,10-perylenequinone (150 mg) was dissolved in 150 ml of warm, glacial acetic acid, the solution was cooled to 35 to 40 °C, and an insoluble residue (25 mg) was filtered off. The dark-brown filtrate was

then introduced onto a column of silica gel (5 × 50 cm, 100 to 200 mesh), which was eluted with glacial acetic acid by the technique described elsewhere [6]. The fast-moving, light-yellow zone (A), composed primarily of compounds 1 and 8, was followed by a slow-moving, deep-yellow zone (B), composed of dione 2; the next zone (C) was yellow-brown and mainly contained compound 6.

The deep-yellow zone (B) was collected, and concentrated to dryness; yield of crude 2, 65 to 70 mg (43-47%); mp 380 to 382 °C (dec.). The product was purified by dissolving 50 mg in 100 ml of warm, glacial acetic acid, and filtering the solution into a vigorously stirred mixture of 50 ml of warm, glacial acetic acid and 1 g of Darco activated carbon. (See footnote 2.) Compound 2 was quickly adsorbed onto the carbon, and the solution became colorless after the mixture had been stirred for 2 to 3 min. The carbon (containing adsorbed dione) was filtered off, washed with acetic acid, dried at 50 °C, and extracted with 5 ml of warm nitrobenzene. The extract was kept at room temperature for 1 to 2 hr; compound 2 crystallized as light-yellow needles; 30 mg (20%), mp 390 to 392 °C (dec.); lit. mp 350 °C [4]. This material produced one sharp, yellow spot having a strong, purple-pink fluorescence on a thin-layer chromatogram with 18:1:1 (v/v) benzene-*N,N*-dimethylformamide-acetic acid (solvent B), 75 min, R_f 0.65 ± 0.02.

4. A Simplified Procedure for Purification of 3,10-Perylenequinone (2)

Analytically pure 3,10-perylenequinone is difficult to obtain by fractional recrystallization. However, a product of about 98 percent purity, which can be utilized for many purposes (including oxidation, and reduction to the corresponding diol), may be obtained as follows. A sample of crude 3,10-perylenequinone (400 mg) is successively extracted with benzene in a

Soxhlet apparatus for 6 hr, and then with 150 ml of 4 percent aqueous sodium hydroxide solution by stirring at 40 to 45 °C for 2 hr. The crude dione **2** is then successively recrystallized from 4:1 (v/v) *N,N*-dimethylformamide-glacial acetic acid (50 ml) and warm nitrobenzene (50 ml); yield 240 to 260 mg (60–65%). This product gives a quite satisfactory thin-layer chromatogram and infrared spectrum; the impurity that shows absorption bands at 5.65 and 5.75 μm is diminished to an amount corresponding to *ca.* 98 percent purity.

5. Anthraquinone-1,5-dicarboxylic Acid (**8**)

5.1. Discussion

Anthraquinone-1,5-dicarboxylic acid (**8**) [7] may be prepared by oxidation of perylene or 3,10-perylenequinone with chromic acid [4, 8]; or by oxidation of 3,9-perylenequinone with chromic anhydride in sulfuric acid [9]; it may be characterized as its dimethyl ester [10].

5.2. Preparation of Anthraquinone-1,5-dicarboxylic Acid (**8**)

The dark-brown filtrate obtained after separation of **2** (see sec. 3.2) was kept at room temperature for 48 hr, to yield crude **8**, 50 mg (4.8%). The crude product (50 mg) was dissolved in about 10 ml of 10 percent aqueous ammonium hydroxide, the solution was filtered, and the cold filtrate was acidified with dilute hydrochloric acid. The precipitated acid (**8**) was further purified by recrystallization from aqueous methanol (with concentration and cooling) to yield colorless or pale-yellow, lustrous crystals of **8**; yield 35 mg (3.3%); mp 388 to 390 °C (sintering at 340 °C, anhydride formation). A thin-layer chromatogram (silica gel G, 250 μm thick) showed a colorless to pale-yellow spot having light-blue fluorescence, solvent A, 60 min, R_f 0.32 \pm 0.02.

6. 4-Oxo-4*H*-benz[*de*]anthracenedicarboxylic Anhydride (**6**)

6.1. Discussion

4-Oxo-4*H*-benz[*de*]anthracenedicarboxylic anhydride (**6**) ("peryleneic acid") may be prepared by exhaustive oxidation of perylene (**1**) with chromic acid [11, 12], by oxidation of 3,10-perylenequinone (**2**) with either manganese dioxide in concentrated sulfuric acid [11] or potassium permanganate in pyridine [5], or by oxidation of perylene (**1**) with hydrogen peroxide-vanadium pentoxide complex as described in sec. 6.3.

6.2. Preparation of 4-Oxo-4*H*-benz[*de*]anthracenedicarboxylic Anhydride (**6**)

To a stirred solution of crude 3,10-perylenequinone (**2**) (1 g; 0.0035 mole) in 50 ml of concentrated sulfuric

acid (cherry-red solution) at 95 °C was added, portionwise, 6 g of active manganese dioxide during 1 hr. The brown-red solution was cooled, and poured into ice water (400 ml), and the precipitate was filtered off; yield of crude **6**, 250 to 300 mg (23.7–28.4%). The crude mixture was extracted with 150 ml of warm 4 percent aqueous sodium hydroxide at 45 to 50 °C for 2 hr, and the suspension was filtered. On acidification with dilute hydrochloric acid, the filtrate, which showed a deep-green fluorescence, yielded 200 mg (19%) of crude **6**. The crude acid (**6**) was dissolved in 150 ml of warm, glacial acetic acid, the solution was filtered, and the filtrate was chromatographed on a column (5 x 50 cm) of silica gel with glacial acetic acid as the eluant. The second zone (brown-yellow) was collected, and evaporated to dryness; the product was refluxed with acetic anhydride for 30 min, and the extract was evaporated to dryness. Recrystallization from nitrobenzene-pentane yielded orange-yellow crystals of **8**, 60 mg (5.7%), mp 335 to 337 °C (dec.). A thin-layer chromatogram showed a yellow to yellow-orange spot having a light-blue fluorescence; solvent B, 60 min, R_f 0.57 \pm 0.02.

6.3. Oxidation of Perylene With Hydrogen Peroxide-Vanadium Pentoxide Complex

To a solution of perylene (**1**) (0.5 g; 0.002 mole) in 200 ml of glacial acetic acid at 100 °C was added dropwise, with stirring, the yellow complex prepared by dissolving 100 mg of vanadium pentoxide in 10 ml of 50 percent hydrogen peroxide; a vigorous reaction ensued, and the solution turned blue-purple. After addition was complete (10 min), the mixture was stirred at room temperature for 60 min; then 50 ml of water was added, and the mixture was stirred for 15 min, and concentrated to about 50 ml. The resulting precipitate (300 mg) was stirred with warm 4 percent aqueous sodium hydroxide for 2 hr, and the suspension was filtered; the filtrate was acidified with dilute hydrochloric acid, to give crude **6** (200 mg, 33.9%). This product was purified by column chromatography on silica gel as described in sec. 6.2; the yield of **6** was 95 mg (16.1%). A thin-layer chromatogram was identical with that of the product described in sec. 6.2.

7. Phenanthrene-1,8,9,10-tetracarboxylic Dianhydride (**7**)

7.1. Discussion

Compound **7** may be prepared by oxidation of compound **6** with nitric acid [12].

Compound **7** was prepared by a modification of the procedure of Brown and Todd [5]. Use of *N,N*-dimethylformamide as a cosolvent in the oxidation enhanced the solubility of the starting material, dione **2**, and resulted in a higher yield of **7**.

7.2. Preparation of Phenanthrene-1,8,9,10-tetracarboxylic Dianhydride (7)

A mixture of compound **2** (400 mg; 0.0014 mole), finely powdered potassium permanganate (1 g), *N,N*-dimethylformamide (50 ml), pyridine (10 ml), acetic acid (5 ml), and 3 ml of water was heated at 100 °C for 30 min, and filtered hot from the precipitate of manganese dioxide. The brownish filtrate was cooled, and a small amount of the starting material separated; this was filtered off, and the filtrate was saved. The manganese dioxide was extracted with 150 ml of 4 percent aqueous sodium hydroxide at 50 °C for 2 hr, and the suspension was filtered. The two filtrates were combined, cooled, acidified with dilute hydrochloric acid, and kept overnight at room temperature, affording crystals that were reextracted with base and reprecipitated from the extract, affording crude dianhydride **7** (80–100 mg) (17.8–22.2%); this was purified by column chromatography on silica gel. Elution with 9:1 (v/v) glacial acetic acid–2-butanone gave a yellow zone, which was collected, and evaporated to dryness. The product was recrystallized from acetic anhydride (35 ml), to yield pale-yellow to orange-yellow crystals of dianhydride **7**, yield 30 mg (6.6%); mp 362 to 364 °C (dec.). A thin-layer chromatogram on Silica Gel G (250 μm thick) showed a pale-yellow spot having a strong blue-green fluorescence, solvent B, 75 min, R_f 0.22 ± 0.04.

8. 2,11-Dihydroxy-3,10-perylenequinone (4)

8.1. Discussion

2,11-Dihydroxy-3,10-perylenequinone was prepared by Friedel–Crafts condensation of 1,2-naphthoquinone by a modification of the procedure of Zinke and co-workers [13].

8.2. Preparation of 2,11-Dihydroxy-3,10-perylenequinone (4)

A mixture of finely powdered 1,2-naphthoquinone (2 g), sodium chloride (2 g), and anhydrous aluminum chloride (15 g) was placed in a round-bottomed flask (protected with a drying tube) and was heated in an oil bath at 140 to 145 °C for 3 hr. The mixture was cooled, cautiously treated with 6 *N* hydrochloric acid, and refluxed for 5 to 10 min; the resulting dark-purple solid was filtered off, washed with water, and dried, yield of crude **4**, 1.89 g (94.5%). The product was recrystallized in the following way: crude product (800 mg) was heated, with stirring, with 280 ml of nitrobenzene, and the suspension was filtered while hot; the product crystallized out on cooling the filtrate. It was redissolved by heating, and the solution was cooled to about 40 °C; the product was filtered off, washed successively with nitrobenzene, benzene, and methanol, and dried in a vacuum desiccator, giving lustrous, green-purple crystals of **4**; yield 200 mg

(25%), mp 432 to 435 °C (dec.). The sample was recrystallized once more for analysis.

A thin-layer chromatogram showed a purple-pink spot when the solution was dilute, and a deep-blue spot when the solution was concentrated (weak-purple fluorescence, changing to a blue fluorescence, under ultraviolet light illumination for 2–3 min); silica gel G, 200 μm thick, 8:1:1 (v/v) toluene–*N,N*-dimethylformamide–acetic acid (solvent C), 8 min, R_f 0.48 ± 0.03.

9. 4,9-Dihydroxy-3,10-perylenequinone (5)

9.1. Discussion

4,9-Dihydroxy-3,10-perylenequinone (**5**) can be prepared by hydrolysis of 3,4,9,10-tetranitroperylene [14, 15], followed by air oxidation of the 3,4,9,10-perylene-tetrol obtained [15].

9.2. Preparation of 4,9-Dihydroxy-3,10-perylenequinone (5)

A solution of 3,4,9,10-tetranitroperylene in concentrated sulfuric acid was heated in the air at 140 °C for 6 hr [14, 15]. The product was twice recrystallized from nitrobenzene, and then sublimed at 400 °C/0.05 mm, to give lustrous, blue-black crystals, mp 480 to 485 °C (with sublimation and some decomposition). A thin-layer chromatogram (silica gel G, 200 μm thick) showed an olive-brown spot having a strong, purple fluorescence, relatively stable to short illumination by ultraviolet light; solvent C, 8 min, R_f 0.63 ± 0.04.

10. 1,12-Perylenequinone (3)

10.1. Discussion

1,12-Perylenequinone (**3**) was prepared by oxidation of crude 1,12-perylenediol with air and then with lead dioxide, following the procedure of Zinke and Hanselmayer [16]. It has been found in this laboratory, however, that the above procedure is not very efficient, as the desired dione (**3**) is a labile compound that is difficult to prepare in quantity and to purify. Purification of dione **3** by fractional recrystallization, as described in reference [16], does not afford a homogeneous product, as is evident from thin-layer chromatograms (see sec. 10.6). The procedure for the purification of dione **3** described here involves two chromatographic separations: (a) on silica gel and (b) on neutral alumina. Dione **3**, obtained in very low yield, has been found to have a melting point (215–217 °C) considerably lower than that reported (287 °C) [16]; it gave a satisfactory elementary analysis, and yielded the known [16] 1,12-dibenzoyloxyperylene on reductive benzylation.

The starting material (1,12-perylenediol) was prepared by a sequence of reactions, including oxidative dimerization of 2-naphthol to 1,1'-bi-2-naphthol, conversion of the latter into the corresponding dimethyl

ether, and cyclization and demethylation of the ether intermediate to 1,12-perylenediol. The preparation of the reaction intermediates is described in the following subsections.

10.2. Oxidative Dimerization

A stirred solution of 2-naphthol (25 g; 1.73 moles) in 400 ml of methanol and 300 ml of water was treated, in portions, with an aqueous solution (100 ml) of ferric chloride hexahydrate (50 g; 1.85 mole) at 55 °C during 5 to 7 min; stirring was continued for 45 min at 50 to 52 °C. At this point, the product crystallized out from the green mixture; the mixture was cooled to about 20 °C, and the product was filtered off, washed with ice-cold 3:1:1 (v/v) water-methanol-acetone, and dried in a vacuum oven at 50 °C for 48 hr; yield of the first crop of 1,1'-bi-2-naphthol (white, or slightly pale-greenish needles), 14.1 g, mp 205 to 208 °C. Concentration of the filtrate, and further dilution with water and cooling, yielded a second crop of lower quality (4.2–4.5 g). The product was recrystallized once from water-methanol-acetone (decolorizing carbon), and this product (mp 212–214 °C) was used in the next step.

An analytical sample was obtained by twice recrystallizing the product from glacial acetic acid, to give snow-white, lustrous crystals; dried at 140 °C/0.05 mm for 3 hr, mp 216 to 218 °C; the solidified melt had mp 219 to 220 °C; lit. mp 218 °C [17]. Increase in concentration of the ferric chloride, or of the starting material, did not improve the yield of the product, but gave a colored product; the dilute solution seemed to be important for the success of the oxidative dimerization reaction; ν_{\max}^{KCl} 3509(w); 3448(s); 3058(w); 1624(s); 1592(s); 1515(s); 1466(s); 1435(m); 1408(sh); 1385(s); 1351(w); 1321(m); 1279(m); 1253(s); 1217(s); 1174(s); 1144(s); 1124(w); 1070(sh); 1020(w); 982(m); 954(m); 948(sh); 935(m); 868(m); 830(s); 820(sh); 799(sh); 776(m); 767(s); 722(m); 676(m) cm^{-1} .

10.3. Methylation

Once-recrystallized³ 1,1'-bi-2-naphthol (mp 210–212 °C, 10 g) was dissolved, with stirring, in 8 percent aqueous sodium hydroxide (100 ml) containing 2 g of sodium hydrosulfite; the solution was treated dropwise with methyl sulfate (15 ml) at 55 °C in a hood; the dimethyl ether crystallized out after 15 to 30 min of stirring. The reaction mixture was cooled and filtered, and the solid was washed with water, and dried in a vacuum desiccator. The yield of crude 2,2'-dimethoxy-1,1'-binaphthyl was 8.8 g (82.8%). A sample recrystallized from 4:1 (v/v) acetic acid-ethanol and dried at 110 °C/0.05 mm for 3 hr had mp 190 to 191 °C; lit. mp 190 °C [18]; ν_{\max}^{KCl} 3086(w); 2959(w); 2858(w); 1618(s); 1592(s); 1503(s); 1475(sh); 1460(s); 1440(sh);

³ If crude starting material was used, the methylation product had an extremely strong fragrance due to formation of 2-methoxynaphthalene.

1430(w); 1389(sh); 1370(sh); 1371(m); 1319(m); 1266(s); 1249(s); 1212(sh); 1177(m); 1149(m); 1134(m); 1089(s); 1064(s); 1050(w); 1020(m); 966(w); 942(sh); 899(s); 868(m); 813(s); 796(sh); 782(m); 757(w); 747(s); 708(m); 678(m) cm^{-1} .

10.4. Cyclization

A mixture of dry, powdered, recrystallized 2,2'-dimethoxy-1,1'-binaphthyl (10 g; 0.033 mole), sodium chloride (5 g), and anhydrous aluminum chloride (35 g) was placed in a round-bottomed flask, protected from moisture, and heated at 165 °C for 90 min. The dark-green mixture was cooled, and carefully treated with warm 2.5 *N* hydrochloric acid containing 2 g of stannous chloride; after the mixture has been briefly warmed, the black-green solid was filtered off, washed with 2.5 *N* hydrochloric acid, and dried over sodium hydroxide in a vacuum desiccator. The yield of crude 1,12-perylenediol was 8–8.5 g (85–91%). Inspection of the crude product by thin-layer chromatography showed the presence of an appreciable proportion of 1,1'-bi-2-naphthol, indicating that the treatment with aluminum chloride caused some demethylation before cyclization to the perylenediol. When the cyclization reaction was conducted in small batches (1 g), and the temperature was gradually raised to 165 °C, the amount of side-product decreased somewhat. The crude product was difficult to purify.

In an attempt at purification, a small sample of crude diol was dissolved in warm *p*-dioxane, and the solution was filtered into 6 *N* hydrochloric acid containing stannous chloride. The light-gray solid that crystallized out was still impure according to a thin-layer chromatogram with 18:1:1 (v/v) benzene-*N,N*-dimethylformamide-acetic acid. Purification of the diol by column chromatography is also difficult, because of the air oxidation that occurs.

10.5. Sodium Hydroxide Extraction and Partial Oxidation of 1,12-Perylenediol

Crude 1,12-perylenediol (5 g; 0.0175 mole) was stirred with 3 percent aqueous sodium hydroxide (1.5 liters) at 55 °C for 60 min; to prevent oxidation of the diol, small portions (4 x 150 mg) of powdered aluminum-nickel alloy (1:1 by weight) were periodically added to the mixture to avoid foaming due to evolution of hydrogen. The reaction mixture (which showed a strong, green fluorescence) was filtered through a layer of filter paper, and the filtrate was partially oxidized by bubbling air through it at room temperature for 12 to 18 hr. The dark-brown solid was filtered off, washed with water, and dried; yield of crude 1,12-perylenequinone, 0.8 g (16.1%). The filtrate was neutralized with concentrated hydrochloric acid, and the dark-brown solid (an additional crop of dione **3**) was isolated; yield 0.9 g; total yield 1.7 g (34.2%). The second crop contained a considerable proportion of 1,12-perylenediol and other hydroxylated impurities.

10.6. Isolation and Purification of 1,12-Perylenequinone (3)

A suspension of crude dione **3** (1 g; 0.0035 mole) and lead dioxide (8 g; 0.033 mole) in 200 ml of dry benzene was refluxed for 2.5 hr, and filtered while hot. The solid was again refluxed with 150 ml of benzene, and the brown-red filtrates were combined and concentrated to about 120 ml. Thin-layer chromatography on silica gel with 18:1:1 (v/v) benzene-*N,N*-dimethylformamide-acetic acid indicated the presence of five components (colored and colorless, but fluorescent). The original filtrate (120 ml) was introduced onto a silica gel column (5×50 cm) and eluted with 4:1 (v/v) benzene-acetic acid (1–1.2 liter; 1 ml per min). Five zones were successively eluted. The slow-moving, dark-red zone was collected, and evaporated to dryness. The solid was treated with 150 ml of hot benzene, and the suspension was filtered, the filtrate being run into a stirred slurry of neutral alumina (75 g) in benzene. The adsorbate with dione **3** was filtered off, and transferred to a column (3×35 cm), and thoroughly washed with warm benzene until the eluate was free from any fluorescent impurity. The orange-red column was then eluted with 1:1 (v/v) benzene-acetone. The eluate was concentrated to about 3 ml, and the solution was filtered. The filtrate was kept for 24 hr at room temperature, giving lustrous, red crystals of 1,12-perylenquinone (**3**); these were filtered off, washed with benzene, and dried; yield 25 mg (2.5%), mp 215 to 217 °C (darkening at 210 °C), lit. mp 287 °C [16]. The sample was dried at 78 °C/0.05 mm for 2 hr, and analyzed.

Anal. Calcd, for C₂₀H₁₀O₂: C, 85.08; H, 3.57. Found: C, 85.20; H, 3.36.

A thin-layer chromatogram (silica gel G, 250 μm thick) showed a homogeneous, orange-red spot having a pink-cherry fluorescence; solvent A, 60 min, *R_f* 0.12±0.02; solvent B, 75 min, *R_f* 0.61±0.02. A solution of dione **3** (10 mg) in *p*-dioxane (1 ml) was treated at 40 °C with 5 ml of 10 percent aqueous sodium hydroxide containing 300 mg of sodium hydrosulfite and 0.25 ml of benzoyl chloride. Concentration and cooling produced greenish-yellow crystals (strong, green fluorescence). The product was dissolved in warm methanol (or methanol-acetone) and the filtered solution was treated with Darco carbon (250 mg). The adsorbate of the product on carbon was extracted with warm benzene; the filtered solution was concentrated to 3 ml, and the solution was diluted with ethanol-pentane to turbidity, and kept at room temperature for 24 hr. Yellowish crystals (8 mg) were filtered off, and dried at 110 °C/0.05 mm for 2 hr; mp 225 to 226 °C; the product was identical with an authentic sample of 1,12-dibenzoyloxyperylene [16]; $\lambda_{\text{max}}^{\text{MeOH}}$ 415 (ε ~ 6,000) and 435 nm (ε ~ 7,500). $\nu_{\text{max}}^{\text{KCl}}$ 2958(w); 2873(sh); 1736(s); 1626(sh); 1592(m); 1497(m); 1453(m); 1445(sh); 1373(sh); 1355(m); 1333(sh); 1315(sh); 1255(s); 1218(m); 1205(sh); 1176(m); 1150(sh); 1123(w); 1087(m); 1063(m); 1029(m); 990(sh); 869(m); 826(m); 816(sh); 800(sh); 780(sh); 760(m); 706(s) cm⁻¹.

11. 3,9-Perylenequinone (9)

11.1. Discussion

3,9-Perylenequinone (**9**) may be prepared by hydrolysis of the corresponding dichloro- or dibromoperylene [19], or by oxidation of 1,2,3,7,8,9-hexahydro-3,9-perylenquinone with iodine in pyridine [9]. In the present study, quinone **9** was obtained by hydrolysis of a mixture of 3,9- and 3,10-dichloroperylene; preparation of such a mixture was reported by Pongratz and Eichler [20], but the ratio of the isomers was not determined by them, and they made no use of the mixture.

11.2. Selective Chlorination of Perylene

Perylene was chlorinated by a slight modification of the procedure of Pongratz and Eichler [20].

To a warm solution of perylene (**1**) (2.52 g; 0.01 mole) in 250 ml of benzene was added 2.8 g (0.021 mole) of sulfuryl chloride, and the solution was refluxed for five hr. The dark-brown reaction mixture was then concentrated to about 70 ml (start of crystallization) and chilled, to give yellow product (750 mg); concentration of the filtrate to about 30 ml, followed by cooling, gave an additional crop (150 mg); total, 900 mg (28%). Recrystallization of the first crop (750 mg) from 40 to 45 ml of warm toluene gave lustrous, golden plates, 500 mg, mp 238 to 241 °C; lit. mp 242 to 280 °C [20].

11.3. Hydrolysis and Separation of 3,9- From 3,10-Perylenequinone

Recrystallized dichloroperylene mixture (300 mg; 0.093 mole) and 15 ml of concentrated sulfuric acid in a test tube was heated in an aluminum block at 165 to 170 °C (beginning at 150 °C) for 5 hr; the dark reaction mixture was cooled, and decomposed with ice water to give a lustrous graphite-like solid, consisting of a mixture of 3,9- and 3,10-perylenquinones; yield, 250 mg (95%). Direct recrystallization of this mixture from 4:1 (v/v) *N,N*-dimethylformamide-acetic acid, gave a mixture containing 3,10-perylenquinone in high proportion; the red filtrate contained an appreciable amount of 3,9-perylenquinone.

The crude quinone mixture (150 mg) was separated with difficulty on a column of silica gel with glacial acetic acid as the eluant by the procedure given in section 3.2. The rates of migration of 3,9- and 3,10-perylenquinones in acetic acid (or other solvents tried) were so close that chromatographic separation had to be repeated three times. Concentration of the eluates yielded 32 mg of 3,9-perylenquinone and about 98 mg of 3,10-perylenquinone, corresponding to an approximate weight ratio of 3:1. For analysis, quinone **9** was recrystallized from hot, glacial acetic acid, to give dark-purple needles, mp 372 to 375 °C (dec.) lit. mp 350 °C (dec.) [9].

A thin-layer chromatogram (silica gel G, 250 μm thick, 75 min) of 3,9-perylenequinone (solvent B), showed a dark-purple spot (light-pink fluorescence) R_f 0.63 ± 0.03 , as compared to a yellow spot for 3,10-perylenequinone, R_f 0.65 ± 0.02 .

The best way to distinguish between 3,9- and 3,10-perylenequinone is by means of their characteristic visible spectra in *N,N*-dimethylformamide. In this solvent, 3,10-perylenequinone shows peaks at 353, 395, and 415 nm, whereas 3,9-perylenequinone shows peaks at 429, 523, and 566 nm; quinone **2** shows no absorption above 415 nm.

The infrared absorption spectrum of **9** shows the following major absorption bands: $\nu_{\text{max}}^{\text{KCl}}$ 2912(w); 1658(s); 1600(m); 1448(ml); 1391(m); 1350(m); 1301(m); 1268(m); 1208(m); 1187(m); 1142(m); 1100(m); 834(m); 741(w); 705(w) cm^{-1} .

12. Spectrophotometric Measurements

12.1. Apparatus

The infrared spectra were recorded in potassium chloride pellets with a Perkin-Elmer Infracord Model 137 (see footnote 2) and a Model 257 grating spectrophotometer (see footnote 2), which were calibrated against a polystyrene standard or against the Nujol (see footnote 2) band at 2861 cm^{-1} . Ultraviolet and visible spectra were recorded with a Beckman DK-2 spectrophotometer.

12.2. Discussion of Spectra

The infrared absorption spectra of polycyclic, aromatic carboxylic anhydrides show a characteristic doublet in the carbonyl absorption region, namely at 1776 and 1742 cm^{-1} and at 1779 and 1736 cm^{-1} , and this doublet is shown by compounds **6** and **8**. This split of the anhydride carbonyl band into a doublet has been observed for other acid anhydrides [6, 21], but the doubling of the carbonyl band in nonpolycyclic, aromatic acid anhydrides appears at somewhat longer wavelength (1865 to 1761 cm^{-1}) [22, pp. 127-128].

It may be noted, however, that at least three recrystallizations of compound **7** from hot acetic anhydride were necessary to convert some C=O absorption at 1697 cm^{-1} (due to the free carboxyl group) into the anhydride doublet.

The carbonyl absorption of compound **9** is found at 1689 cm^{-1} , which is normal for aromatic acids [22, p. 162]. The infrared absorption spectra of 3,9-, 3,10-, and 1,12-perylenequinones show carbonyl absorption in the region of 1667 to 1613 cm^{-1} , typical of polycyclic, aromatic quinones [6; 22, p. 151]. A transparent region is found between 1111 and 909 cm^{-1} for 3,9- and 3,10-perylenequinones, resembling those observed for the (*para*) 1,6- and 1,8-pyrenedione [6]; on the other hand,

moderate to strong absorption bands are observed for 1,12-perylenequinone in the same region (1111 to 909 cm^{-1}), resembling the (*ortho*) 4,5-pyrenedione [6].

The infrared spectrum of **4** shows a strong hydroxyl group absorption at 3333 cm^{-1} , and aromatic quinone bands at 1642 and 1615 cm^{-1} . The spectrum of **5** shows a very weak hydroxyl group absorption, typical of a chelated structure [22, p. 107]; the spectrum also shows a hydrogen-bonded carbonyl absorption at 1638 cm^{-1} [22, p. 144]; moreover, compound **5** shows all of the chemical reactions of the chelated hydroxyl group, similar to that described for streptovaricin [23]. However, all attempts failed to confirm a chelate ring-structure for **5** by nmr spectroscopy, because of the insolubility of **5** in *N,N*-dimethylformamide, methyl sulfoxide, and other solvents, even at elevated temperature.

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13. References

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