467. 1 : 8 : 9-*Naphthanthr*-10-*one.*

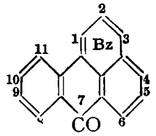
By William Bradley and F. K. Sutcliffe.

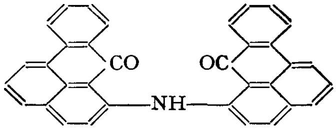
The fact that direct hydroxylation and amidation of *meso*benzanthrone yield only monosubstitution products is ascribed to neutralisation of the effect of the carbonyl group by hydroxyl and amino-substituents which conjugate with the nucleus, but derivation of a simple rule is complicated by the preference of anionoid reagents for either the *ortho*- or the *para*-position relative to the carbonyl group. In this connection 1 : 8 : 9-naphthanthr-10-one is interesting as it possesses two free positions *ortho* and two *para* to the carbonyl group; its direct hydroxylation affords a "*p*-" monohydroxy-derivative, the promoting effect of the carbonyl group being neutralised by the single hydroxyl substituent.

1 : 8 : 9-Naphthanthr-10-one affords a monobromo-derivative which resembles 3-bromo*meso*benzanthrone in yielding a blue quinonoid diketone when it is heated with alcoholic potassium hydroxide at 115—120°. 1 : 8 : 9-Naphthanthr-10-one, unlike *meso*benzanthrone, undergoes no change at this temperature, but fusion with potassium hydroxide at 240—250° affords a bluish-black quinonoid diketone resembling violanthrone. Further bromination of 1 : 8 : 9-naphthanthr-10-one yields a product approximating in composition to a dibromo-derivative. The constitutions of the monohydroxy-, monobromo-, and dibromo-derivatives are discussed, and those of the two isomeric quinonoid diketones.

Although *meso*benzanthrone (I) is preferentially halogenated and nitrated in the *Bz*-nucleus, direct replacement of hydrogen by hydroxy-, amino-, or piperidino-groups occurs at the 4- and 6-positions (Bradley, *J.*, 1937, 1091; 1948, 1175; Bradley and Jadhav, *J.*, 1937, 1791; 1948, 1622). By appropriate choice of conditions the monohalogenated *meso*benzanthrones can be further halogenated and nitrated (Cahn, Jones, and Simonsen, *J.*, 1933, 444; Nakanishi, *Chem. Abst.*, 1932, **26**, 4335) and the mononitro*meso*benzanthrones further nitrated (Pieroni, *Ann. Chim. appl.*, 1931, **21**, 155). When, however, the substituting agent is an anion the limit of substitution is the mono-derivative in the great majority of instances. For example, *meso*benzanthrone heated with potassium hydroxide and an oxidant affords 4- and 6-hydroxy*meso*benzanthrones (Perkin and Spencer, *J.*, 1922, 479; Bradley and Jadhav, *J.*, 1937, 1791), and direct amidation affords 6-amino*meso*benzanthrone and 6 : 6′-di*meso*benzanthronylamine (II), but polyamino-*meso*benzanthrones are not encountered (Bradley, *J.*, 1948, 1175). The result is expected because the effect of an *o*- or *p*-amino- or -hydroxyl substituent is to neutralise the effect of the carbonyl group on which the capacity for anion-substitutions depends.

(I.)





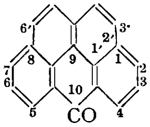
(II.)

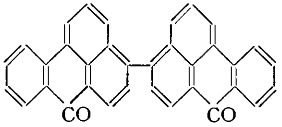
Monosubstitution by anions in aromatic compounds containing single cationoid substituents appears to be a common though not an invariable rule. Nitrobenzene affords a mixture of two monohydroxy-derivatives with potassium hydroxide (Wohl, *Ber.*, 1899, **32**, 3486; 1901, **34**, 2444) and mono-derivatives with potassiocarbazole (G. and M. de Montmollin, *Helv. Chim. Acta*, 1923, **6**, 94) and sodamide–piperidine (Bradley and Robinson, *J.*, 1932, 1254); α- and β-nitronaphthalenes behave similarly (Meisenheimer and Patzig, *Ber.*, 1906, **39**, 2533; Bradley and Robinson, *loc. cit.*).

When two cationoid groupings are present disubstitution products are commonly formed. Anthraquinone and potassium hydroxide yield alizarin; benzoquinone and aniline afford 2 : 5-dianilinobenzoquinone.

In considering the application of a rule relating the number of activating groups to the number of nuclear substitutions effected, account must be taken of the fact that most substituents preferentially enter either the *ortho-* or the *para*-position to the activating group. *meso*Benzanthrone yields 4-hydroxy- and 4-piperidino-*meso*benzanthrones but 6-amino- and 6-alkyl-*meso*benzanthrones. Nitrobenzene yields *o*-nitrophenol but *p*-nitrophenylcarbazole. Similarly, alkylquinolinium halides yield 1-alkyl-1 : 2-dihydro-2-hydroxyquinolines with alkali hydroxides (Decker, *Ber.*, 1892, **25**, 443, 3326), but 1-alkyl-4-cyano-1 : 4-dihydroquinolines with alkali cyanides (Kaufmann and Albertini, *ibid.*, 1909, **42**, 3776; Kaufmann and Widmer, *ibid.*, 1911, **44**, 2058). An opportunity to test the validity of such a rule occurs in 1 : 8 : 9-naphthanthr-10-one (III), a monoketone having two free positions *ortho* and two *para* to the carbonyl group, whose constitution permits disubstitution by anions unrestricted by considerations of preferred orientation.

(III.)



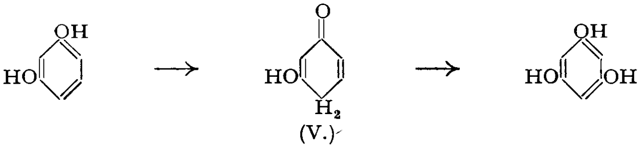


(IV.)

1 : 8 : 9-Naphthanthr-10-one was prepared by Scholl and Meyer (*Ber.*, 1936, **69**, 152) and by Vollmann, Becker, Corell, Streeck, and Langbein (*Annalen*, 1937, **531**, 155) who proved its constitution. Scholl and Meyer recorded the formation of dinitro- and dibromo-derivatives. In the present investigation it was found that 1 : 8 : 9-naphthanthr-10-one and bromine formed a dark, red-brown product, approximating in composition to $C_{19}H_{10}OBr_4$, which yielded 1 : 8 : 9-naphthanthr-10-one when heated with alcohol, pyridine, dilute aqueous sodium hydroxide or sodium hydrogen sulphite, but when kept or heated gave a dibromo-1 : 8 : 9-naphthanthr-10-one. Equimolecular amounts of bromine and 1 : 8 : 9-naphthanthr-10-one in hot nitrobenzene afforded a monobromo-derivative which for the reason given is considered to be the 3'-bromo-compound. The constitution of the dibromo-derivative was not determined but considerations of symmetry suggest that it is probably 3' : 6'-dibromo-1 : 8 : 9-naphthanthr-10-one.

Unlike *meso*benzanthrone which yields 4 : 4'-di*meso*benzanthronyl (IV) when heated with alcoholic potassium hydroxide at 110° (Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**. 259), 1 : 8 : 9-naphthanthr-10-one is unchanged by these reagents even at 125°, showing thus its lower reactivity towards substitution by anions. At 230—240°, 1 : 8 : 9-naphthanthr-10-one readily affords a monohydroxy-derivative when heated with manganese dioxide and potassium hydroxide, but more highly hydroxylated derivatives are not formed. The hydroxy-derivative resembles 4- and differs from 6-hydroxy*meso*benzanthrone in forming an acetate but not a boroacetate, in dissolving readily in aqueous sodium hydroxide, and in the yellow colour and green fluorescence of its aqueous alkaline solution. It is considered to be 2-hydroxy-1 : 8 : 9-naphthanthr-10-one. Under the conditions described 1 : 8 : 9-naphthanthr-10-one approaches *meso*benzanthrone in reactivity.

The absence of dihydroxy-derivatives shows clearly the ability of a hydroxyl substituent to neutralise the effect of a *para*-carbonyl substituent in promoting nuclear substitution by anions. The result harmonizes with the known formation of alizarin from either anthraquinone or 2-hydroxyanthraquinone by the action of alkali and an oxidant (Minaev and Fedorov, *Chem.*

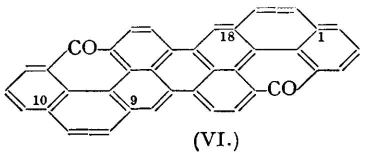


(V.)

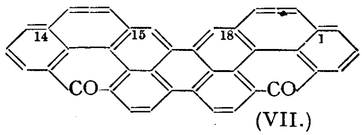
Abs., 1929, **23**, 3701; Il'inski and Nikolayeva, Il'inski and Perelman, *ibid.*, 1937, **31**, 682; Graebe and Liebermann, *Annalen*, 1871, **160**, 130, 135; Liebermann, *ibid.*, 1876, **183**, 145, 169, 184, 203, 213; Baeyer and Caro, *Ber.*, 1874, **7**, 968, 972; Perkin *J.*, 1870, **23**, 133; 1874, **27**, 401), but it suggests that when trihydroxyanthraquinones result from the alkali fusion of dihydroxyanthraquinones additional carbonyl groups are formed at intermediate stages as a result of prototropic changes. Bradley and Robinson (*J.*, 1932, 1255) suggested that phloroglucinol was formed in the alkali fusion of resorcinol as a result of the hydroxylation of the keto-form (V), and the same process may account for the further hydroxylation of the dihydroxyanthraquinones.

Heated with alcoholic potassium hydroxide at 115—120°, 3′-bromo-1 : 8 : 9-naphthanthr-10-one affords a blue, halogen-free diketone having the properties of a quinone. It is insoluble in water or dilute aqueous sodium hydroxide, but it dissolves when sodium dithionite (hydrosulphite) is added. The absorption spectrum of a solution in concentrated sulphuric acid resembles that of *iso*violanthrone(*iso*dibenzanthrone). *iso*Violanthrone results when 3-bromo-*meso*benzanthrone is heated with alcoholic potassium hydroxide (Lüttringhaus and Neresheimer, *loc. cit.*), and the formation of a similar colouring matter from a monobromo-1 : 8 : 9-naphthanthrone suggests that the colouring matter is 9 : 10-18 : 1-bisbenz*iso*violanthrone (VI), and that the monobromo-1 : 8 : 9-naphthanthr-10-one is the 3′-bromo-derivative corresponding in structure to 3-bromo*meso*benzanthrone. It may be remarked that 3-bromo*meso*bezanthrone is the first product of bromination of *meso*benzanthrone as 3′-bromo-1 : 8 : 9-naphthanthr-10-one is of 1 : 8 : 9-naphthanthr-10-one.

According to Vollmann *et al.* (*loc. cit.*), heating 1 : 8 : 9-naphthanthr-10-one with alkali hydroxides results in the formation of a blue colouring matter. The present work has shown that the product contains the 2-hydroxy-1 : 8 : 9-naphthanthr-10-one recorded above, a bluish-black quinonoid diketone $C_{38}H_{16}O_2$, and a more highly oxidised substance the composition of which approximates to $C_{38}H_{18}O_6$. The diketone, although insoluble in warm dilute aqueous sodium hydroxide, dissolved sparingly in alkaline dithionite, forming a bluish-green solution. In concentrated sulphuric acid it gave a violet solution, the absorption spectrum of which differed from that of (VI) and resembled that of violanthrone. For these reasons the diketone is regarded as 14 : 15-18 : 1-bisbenzoviolanthrone (VII).



(VI.)



(VII.)

The third product, $C_{38}H_{18}O_6$, showed the properties of a quinone in that it dissolved in alkaline dithionite; its composition and quinonoid character suggest that it may be a tetrahydroxy-derivative of (VII).

EXPERIMENTAL.

Measurements of absorption spectra were made on a Barfit Hilger Nutting Spectrophotometer Type H. 410. The values of the extinction coefficients (*E*) are the readings on the scale of the instrument for 0·002% solutions in AnalaR sulphuric acid in a 2-cm. cell.

1 : 8 : 9-*Naphthanthr*-10-*one* (cf. Scholl and Meyer, *loc. cit.*).—Finely ground pyrene (200 g.; m. p. 148—149°) and then glycerol (320 c.c.) were added at 70—80° to a mixture of 95% sulphuric acid (2620 c.c.) and water (900 c.c.). The mixture was stirred for 3 hours on the steam-bath, then cooled and added to water (5 l.). The tarry precipitate was collected by decantation and stirred at 70—80° with water (4 l.), and 15% aqueous sodium hydroxide was added to permanent alkalinity. The residual brownish-yellow powder, collected, washed with water, and dried at 100° (114 g.), was then powdered finely and exhaustively extracted by acetone; the extract afforded 55 g. of brown crystals; these were dissolved at 100° in toluene (1 l.), and treated at that temperature with four successive 40-g. quantities of activated alumina, each being stirred in, filtered off, and washed with hot toluene (50 c.c.). The toluene solution, now pale, afforded orange-brown material (35 g.), m. p. 225—235°, on cooling. Two recrystallisations from boiling toluene (500 c.c.) gave orange-yellow needles (25 g.), m. p. 241—243° (Scholl and Meyer, *loc. cit.*, record m. p. 243°). The combined toluene mother-liquors were passed through a column of alumina. The chromatogram, when developed with the aid of toluene (500 c.c.), gave a broad orange-brown band of naphthanthr-10-one, a pale more mobile, yellow band, and a reddish-brown and a dark brown band, both more strongly adsorbed. The naphthanthr-10-one was eluted with toluene, recovered, and recrystallised from toluene (yield, 17 g.; m. p. 241—243°). The two portions of naphthanthr-10-one were united (42 g.) and again crystallised from toluene before use. Further crystallisation gave the pure material, m. p. 246—247°. A dilute solution in concentrated sulphuric acid was pink; it showed maximum light absorption at 4720° (*E*, 1·56) and 5540 A. (*E*, 0·58).

Oxidation. With chromium trioxide in 80% acetic acid 1 : 8 : 9-naphthanthr-10-one afforded 1 : 8 : 9-naphthanthronequinone as reported by Vollmann *et al.* (*loc. cit.*). No characteristic product resulted on oxidation with potassium permanganate in aqueous pyridine.

Bromination of 1 : 8 : 9-*Naphthanthr*-10-*one*.—(a) An excess of bromine added to a solution of naphthanthr-10-one in warm acetic acid produced a dark, reddish-brown precipitate; no hydrogen bromide was evolved. Recrystallisation of the product (m. p. 200—240°) from alcohol or pyridine, or warming with dilute sodium hydroxide solution, yielded unchanged naphthanthr-10-one.

(b) 3′-*Bromo*-1 : 8 : 9-*naphthanthr*-10-*one*. A solution of naphthanthrone (5 g.) and bromine (6·4 g.) in nitrobenzene (50 c.c.) containing carbon tetrachloride (0·5 c.c.) was heated under reflux for 2 hours. Hydrogen bromide was evolved and the liquid became almost colourless. On cooling, a dark brown solid separated (4·5 g.; m. p. 275—285°, after being washed with alcohol). The mother-liquors, steam-distilled, afforded material (2·4 g.), m. p. 240—253°. The two products were united and crystallised from toluene. The following fractions resulted: (A), m. p. 289—294° (2·6 g.); (B), m. p. 265—269° (1·4 g.); and (C), m. p. 200—250° (0·7 g.), consisting mainly of naphthanthr-10-one.

Fraction (A), stirred with chlorobenzene (500 c.c.), afforded a residue (m. p. 310—318°; 0·6 g.) and a solution. The latter was passed through a column of alumina, and the chromatogram was developed by chlorobenzene (600 c.c.) and, finally, chlorobenzene (500 c.c.) containing 0·5% of acetone. The main orange-yellow band was eluted by hot chlorobenzene (20 vols.)–methanol (1 vol.), and the product was recovered by concentration of the extracts. It separated as a yellow solid, m. p. 275—283° after shrinkage at 265°. It was combined with fraction (B) and stirred with toluene (500 c.c.), and the insoluble material (m. p. >300°; 0·5 g.) removed. The solution was passed through alumina and the chromatogram was developed by toluene (2 l.). The main band (yellow) was extracted (Soxhlet) by 200 c.c. of acetone–methanol (4 : 1 by vol.). On cooling, the filtered solution afforded yellow needles (1·7 g.), m. p. 272—274° (Found: C, 67·3; H, 2·6; Br, 25·6. Calc. for $C_{19}H_9OBr$: C, 68·5; H, 2·6; Br, 24·0%). The analytical results suggest that the product is a monobromonaphthanthr-10-one containing 9·4 mols. % of a dibromonaphthanthr-10-one. (Calc. for $0·906C_{19}H_9OBr + 0·094C_{19}H_8OBr_2$: C, 67·3; H, 2·5; Br, 25·4%). Further recrystallisation from *o*-dichlorobenzene raised the m. p. to 274—276° and increased the bromine content. (Found: Br, 28·2%). Redissolved in chlorobenzene and again chromatographed on alumina the material, m. p. 272—274°, was recovered by elution with acetone–methanol (4 : 1) unchanged in m. p. and bromine content (Found: Br, 25·8%). A dilute solution of the product in concentrated sulphuric acid was deep pink; absorption max. at 4830 (*E*, 1·58) and 5620 A. (*E*, 0·82).

(c) 1 : 8 : 9-Naphthanthr-10-one (0·404 g.), added to bromine (2 c.c.), reacted vigorously and dissolved. After 30 minutes the mass had become semi-solid. The whole was kept in a closed vessel over solid sodium hydroxide and under reduced pressure. The residual reddish-brown solid (0·746 g.) fumed slightly in air; it had an odour of bromine. Heated for 3 hours in an open vessel at 130° it became yellow (0·59 g.). This product was dissolved in chlorobenzene (250 c.c.), the solution passed through a column of alumina, and the chromatogram developed with chlorobenzene (500 c.c.). The broad orange band was eluted by hot chlorobenzene containing a small proportion of alcohol. Yellow needles, m. p. 440° (decomp.) (Found: Br, 31·0%), crystallised from the eluate on cooling. These appeared to consist mainly of a dibromo-1 : 8 : 9-naphthanthr-10-one (Calc. for $C_{19}H_8OBr_2$: Br, 38·9%). The product was added to excess of bromine, the solution left overnight, and the uncombined bromine volatilised by heat. The residue, recrystallised from chlorobenzene, again afforded yellow needles, m. p. above 440° (Found: Br, 43·7%). A dilute solution in concentrated sulphuric acid was bluish-pink; it exhibited absorption max. at 4930 (*E*, 1·06) and 5700 A. (*E*, 0·59).

2-*Hydroxy*-1 : 8 : 9-*naphthanthr*-10-*one*.—An intimate mixture of 1 : 8 : 9-naphthanthr-10-one (10 g.) with an equal weight of precipitated manganese dioxide was added during 10 minutes to a stirred melt of potassium hydroxide (60 g.) and water (6 c.c.) at 220—230°. The melt thickened and it became necessary to raise the temperature to 230—240° to maintain fluidity. After 1 hour at this temperature the black product was cooled, broken up, and then added to water (1 l.). The suspension was aerated at 80—90°, and the resulting fine, black undissolved powder was collected. It was then extracted four times at 80—90° with N-sodium hydroxide. The five alkaline solutions so obtained were acidified, each giving a gelatinous orange precipitate which was collected, washed, and dried. In each case the m. p. was 330—335° after a change from deep orange to yellow at *ca.* 270°; the successive yields were 0·58, 1·34, 0·27, 0·14, and 0·14 g.

The undissolved residue was suspended in dilute sulphuric acid, and the manganese oxide dissolved by sulphur dioxide. A yellow solid remained (7·3 g.; m. p. 247—251°). This was extracted thoroughly with hot benzene; the filtered extract afforded 6 g. of unchanged naphthanthr-10-one. The benzene-insoluble material (1·3 g.) was extracted twice by 0·25N-sodium hydroxide. The first extract, acidified, afforded 0·2 g. of material, m. p. 327—333°, the second extract only a trace of a precipitate. The alkali-insoluble residue was a dark brown, infusible solid (0·6 g.). The seven portions of alkali-soluble material were combined (2·7 g.) and heated under reflux with acetic anhydride (100 c.c.) containing boroacetic anhydride (from 2 g. of boric oxide). The resulting brown solution was filtered; brown crystals (2·4 g.) separated on cooling. These were almost completely soluble in chloroform (100 c.c.); after treatment of the filtered solution with charcoal and evaporation a yellow residue (2·3 g.; m. p. 230—231°) remained. Recrystallisation from acetic anhydride afforded yellow needles, m. p. 230—231° (1·9 g.).

The product (1·5 g.) was insoluble in aqueous sodium hydroxide; when boiled for 2 hours with 0·25N-sodium hydroxide (150 c.c.) it formed a yellow solution with a green fluorescence. Acidification afforded a gelatinous, brown precipitate which, collected, washed, and dried, yielded orange-yellow 2-*hydroxy*-1 : 8 : 9-*naphthanthr*-10-*one* (1·3 g.), m. p. 356—358°, unchanged by further recrystallisation from acetic acid (Found: C, 83·6; H, 3·7. $C_{19}H_{10}O_2$ requires C, 84·4; H, 3·7%). 2-Hydroxy-1 : 8 : 9-naphthanthr-10-one formed a deep yellow solution having a green fluorescence in concentrated sulphuric acid [absorption max. at 5110 A. (*E*, 1·44); min. at 5000 A. (*E*, 1·26)].

In parallel experiments 2-hydroxy-1 : 8 : 9-naphthanthr-10-one (0·1 g.) was heated under reflux for 30 minutes with (*a*) acetic anhydride (5 c.c.) and (*b*) acetic anhydride (5 c.c.) containing boroacetic anhydride (0·05 g.). On cooling, the two solutions deposited the same compound as orange needles, m. p. 230—231°, undepressed on admixture.

9 : 10-18 : 1-*Bisbenz*iso*violanthrone*.—3′-Bromo-1 : 8 : 9-naphthanthr-10-one (0·5 g.; m. p. 272—274°) was heated and stirred for 3 hours at 115—120° (inner temp.) with a solution containing potassium hydroxide (2·5 g.) and potassium acetate (0·25 g.) in ethanol (5 c.c.). The reactants became green immediately; within a few minutes the colour was dark olive-green, and at the end of the reaction blue-green in thin layers and black in bulk. When added to water (50 c.c.) which was then heated to boiling, the reaction product yielded an olive-green solid. This was washed with 1% aqueous sodium hydroxide and finally with water. The alkaline filtrates were orange, with a green fluorescence; acidification afforded only a trace of a pale brown precipitate. The alkali-insoluble material was dried and then extracted with boiling acetone; unchanged 3′-bromonaphthanthr-10-one (0·15 g.) dissolved. The residue was extracted with pyridine. A black substance dissolved which did not melt or dissolve in alkaline dithionite even with the addition of pyridine. The pyridine-insoluble product was a violet-black powder; in warm alkaline sodium dithionite solution containing 10% of pyridine it gave a deep bluish-green solution which was filtered, then aerated at 90—95°, and the precipitate solid was collected and washed with water. The iso*violanthrone* derivative was a violet-black powder (Found : C, 90·1; H, 3·4. $C_{38}H_{16}O_2$ requires C, 90·5; H, 3·2%), soluble in concentrated sulphuric acid with a deep bluish-green colour [absorption max. at 6370 (*E*, 1·41) and 7000 A. (*E*, 2·97)].

Alkali Fusion of 1 : 8 : 9-*Naphthanthr*-10-*one* : *Formation of* 2-*Hydroxy*-1 : 8 : 9-*naphthanthr*-10-*one and* 14 : 15-18 : 1-*Bisbenzoviolanthrone*.—1 : 8 : 9-Naphthanthr-10-one (5 g.; m. p. 243—245°) was stirred at 240—250° for 1·5 hours with a melt of potassium hydroxide (45 g.) and potassium acetate (5 g.). Whilst still molten the product was added to water (1 l.), and the suspension was heated on the water-bath, aerated for an hour, and then filtered. The bluish-black residue was washed several times with hot, dilute sodium hydroxide solution and finally with water. The alkaline filtrates were orange, with a strong green fluorescence. Acidification yielded a brown gelatinous precipitate and this was collected, washed, and dried. The product (0·4 g.), recrystallised from acetic acid, yielded 2-hydroxy-1 : 8 : 9-naphthanthr-10-one, m. p. 353—356°, not depressed by admixture with the compound prepared as above.

The alkali-insoluble bluish-black material (4·2 g.) was extracted for several hours with 1 : 2 : 4-trichlorobenzene–phenol (1 : 1), then filtered. There was a residue (A) (1·7 g.). The extract was concentrated to one-quarter bulk, then cooled, and a black solid (B) collected, washed with benzene, and dried (yield, 2·3 g.); this dissolved in concentrated sulphuric acid with a grey-green colour, in alkaline sodium dithionite with a pale blue colour, and in the same medium containing a small proportion of pyridine with a deep greenish-blue colour.

Fraction B (1 g.) was extracted by boiling trichlorobenzene (250 c.c.). An undissolved residue (0·3 g.) was removed by filtration and the hot filtrate was passed through a column of alumina at 160—170°. Development with boiling trichlorobenzene yielded a succession of bands. The most mobile was a pink band consisting mainly of naphthanthr-10-one. Further development with boiling trichlorobenzene containing 1% of cresols (mixed isomers) resulted in the elution of a pale blue band (solution D). Finally, boiling trichlorobenzene containing 2% of cresols was used; a pale brown band passed through the column, whilst a dark blue band occupied the uppermost one-third. The blue band was separated and the colouring matter eluted by trichlorobenzene–cresols (1 : 1 by vol.). The eluate, filtered, concentrated, and then mixed with toluene, deposited 14 : 15-18 : 1-*bisbenzoviolanthrone* as a blue-black powder (0·063 g.) (Found : C, 89·8; 89·4; H, 3·8, 3·3. $C_{38}H_{16}O_2$ requires C, 90·5; H, 3·2%). It formed in concentrated sulphuric acid a violet solution [absorption max. at 5320 (*E*, 1·76) and 7400 A. (*E*, 1·66)]. It dissolved sparingly in warm alkaline sodium dithionite solution with a bluish-green colour; in the presence of a small proportion of pyridine the intensity of the colour was greatly increased. The solution in hot trichlorobenzene or nitrobenzene was blue with a strong red fluorescence, which in more concentrated solutions almost masked the blue colour. The addition of a small quantity of phenol or cresol completely inhibited the fluorescence.

The by-product present in solution D was recovered by evaporation of the solvent and addition of acetone as a trace of blue-black material, soluble in concentrated sulphuric acid with a grass-green colour [absorption max. at 4880 (*E*, 1·12) and 7400 A. (*E*, 0·87)].

The residue (A) was a black powder, almost insoluble in boiling cresol, but soluble in a warm solution of sodium hydroxide (3 g.) and sodium dithionite (2 g.) in a mixture of water (180 c.c.) and pyridine (20 c.c.). The substance did not dissolve in the absence of pyridine. The solution was filtered and the filtrate aerated. A black precipitate formed and this *substance* was collected and washed (Found : C, 79·1; 79·4; H, 3·3, 3·6. $C_{38}H_{18}O_6$ requires C, 80·0; H, 3·2%). It dissolved in sulphuric acid forming a greyish solution [light absorption : ill-defined max. at 5700 (*E*, 1·0) and 6600 A. (*E*, 1·0)].

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