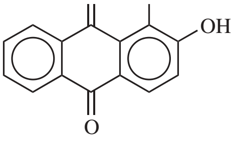
DYES, ANTHRAQUINONE

1. Introduction

Anthraquinone chemistry began in 1868 with the elucidation of the structure of the naturally occurring compound alizarin (**1**) (1,2-dihydroxyanthraquinone) [72-48-0] by C. Graebe and C. Liebermann (**1**).

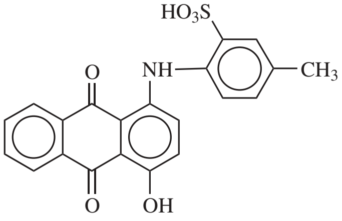


(**1**)

Subsequently, H. Caro and W. H. Perkin independently developed the commercial manufacturing process of alizarin from anthraquinone (qv) through anthraquinone-2-sulfonic acid. Taking advantage of these inventions, many manufacturers came to produce various kinds of hydroxyanthraquinones, which were used as mordant dyes for dyeing cotton and wool.

Mordant dyes have excellent lightfastness. However, their colors are not so brilliant, and they need treatment of fibers with metal salts such as those of Cr, Al, Fe, or Ni before dyeing, which makes the dyeing process complicated and leveling properties unsatisfactory.

In 1894 the first two anthraquinone acid dyes, CI Acid Violet 43 [4430-18-6] (**2**) (CI 60730) and CI Acid Green 25 [4403-90-1] (**3**) (CI 61570) were invented. This encouraged the subsequent development of various kinds of anthraquinone acid dyes, which were used to dye wool in fast, brilliant shades without need for pretreatment.



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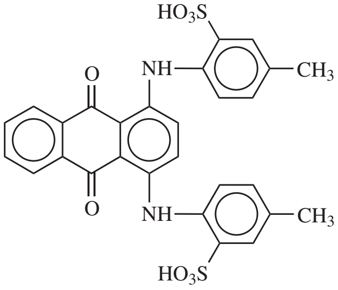


(**3**)

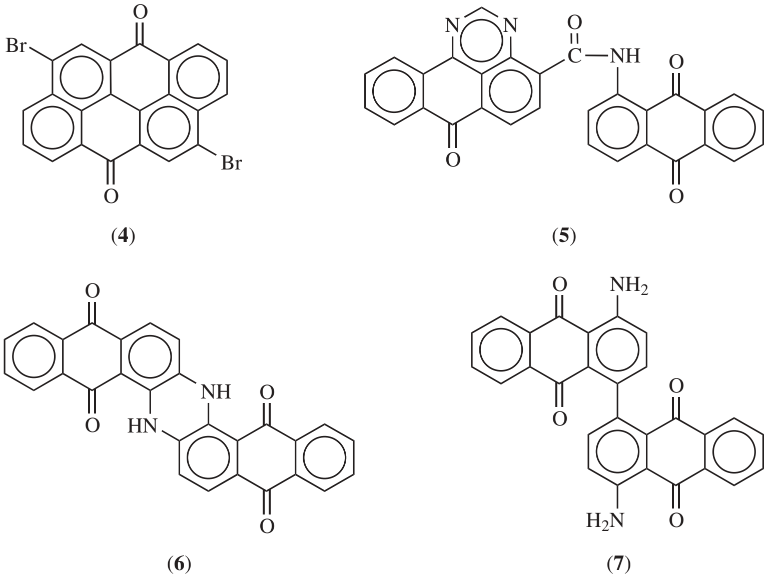
In 1901, mercury catalyzed α-sulfonation of anthraquinone was discovered, and this led to the development of the chemistry of α-substituted anthraquinone derivatives (α-amino, α-chloro, α-hydroxy, and α,α′-dihydroxyanthraquinones). In the same year R. Bohn discovered indanthrone. Afterward flavanthrone, pyranthrone, and benzanthrone, etc, were synthesized, and anthraquinone vat dyes such as benzoylaminoanthraquinone, anthrimides, and anthrimidocarbazoles were also invented. These anthraquinone derivatives were widely used to dye cotton with excellent fastness, and formed the basis of the anthraquinone vat dye industry.

The appearance of synthetic fibers in the 1920s accelerated the further development of anthraquinone dyes. Soon after British Celanese succeeded in commercializing cellulose acetate fiber in 1921, anthraquinone disperse dyes for this fiber were invented by Stepherdson (British Dyestuffs Corp.) and Celatenes (Scottish Dyes) independently. Anthraquinone disperse dyes for polyester fiber were developed after the introduction of this fiber by ICI and Du Pont in 1952. These dyes were improved products of the disperse dyes that had been developed for cellulose acetate fiber 30 years before.

In the 1950s acid dyes were successively developed to dye nylon carpet with excellent fastness and uniform leveling. Development of polyacrylonitrile fiber stimulated the invention of anthraquinone basic dyes, modified disperse dyes in which quaternary ammonium groups are introduced.

Some anthraquinone dyes are employed as organic pigments (see PIGMENTS, ORGANIC). Examples appear in Figure 1. Indanthrone blue (**6**) is an important automotive paint pigment as is CI Pigment Red 177 (**7**), a bisanthraquinonyl.

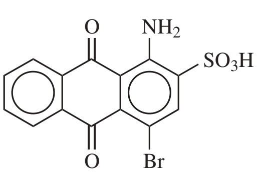
Dyes for cellulose fiber include the direct, sulfur, vat, azoic, and reactive dyes. R&D activities of world dye manufacturers have been focused on the area of reactive dyes, because reactive dyes offer brighter shades and excellent wet-fastness and have been increasingly used for dyeing cotton.



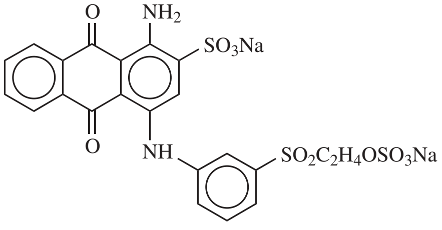
(4) (5) (6) (7)

Fig. 1. Anthraquinone dyes used as organic pigments: (**4**) = dibromoanthanthrone [4378-61-4] (CI Pigment Red 168; CI Vat Orange 3; CI 59300); (**5**) = an anthrapyrimidine [4216-01-7] (CI Pigment Yellow 108; CI Vat Yellow 20; CI 68420); (**6**) = indanthrone blue [81-77-6] (CI Pigment Blue 60; CI Vat Blue 4; CI 69800); (**7**) = a bisanthraquinonyl [4051-63-2] (CI Pigment Red 177, CI 65300).

Production of anthraquinone reactive dyes based on derivatives of bromamine acid (**8**) was first commercialized in 1956. Some improvements have been made and now they are predominantly used among the reactive blue dyes. CI Reactive Blue 19 [2580-78-1] (**9**) (CI 61200) (developed by Hoechst in 1957) has the greatest share among them including dye chromophores other than anthraquinones.



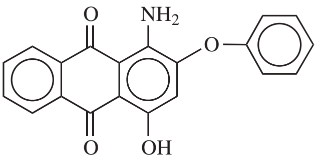
(**8**)



(**9**)

2. Manufacturing Overview

2.1. General. The synthesis of an anthraquinone dye generally involves a large number of steps. For example, CI Disperse Red 60 [17418-58-5] (**10**) (CI 60756) (a typical disperse red dye) requires five steps starting from anthraquinone, and CI Disperse Blue 56 [31810-89-6] (**11**) (CI 63285) requires six steps.



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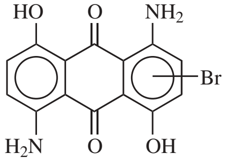
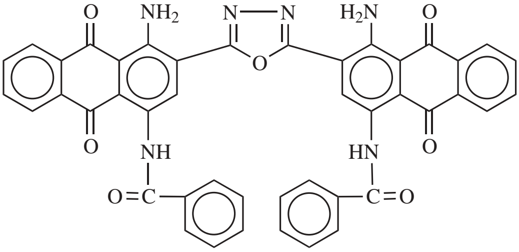


(**11**)

The manufacturing process of anthraquinone vat dyes is more complicated, and, in the extreme case of CI Vat Blue 64 [15935-52-1] (**12**) (CI 66730), requires 11 steps starting from phthalic anhydride.



(**12**)

Highly toxic metals such as mercury or chromium(VI) are sometimes required. Some processes need to employ a large amount of organic solvent, and others involve a great quantity of waste acids. With the increasing demand for environmental protection, the regulation of pollutant effluents has become more stringent year after year, which has caused a sharp increase in the costs for waste-water treatment. This situation has led to intensive improvement of conventional methods and the development of new synthetic routes as well. A typical example is the development of nonpolluting processes for the production of 1-amino-anthraquinone and CI Disperse Blue 56. These compounds have been produced conventionally via anthraquinone-α-sulfonic acid or anthraquinone-α,α′-disulfonic acid prepared by mercury-catalyzed sulfonation of anthraquinone. In 1980 Sumitomo Chemical and Mitsubishi Chemical developed a mercury-free production process for 1-aminoanthraquinone and CI Disperse Blue 56 (11), respectively. These processes involve α-nitration of anthraquinone instead of α-sulfonation.

Efforts have also been made to overcome complicated processes. Methods to reduce the number of steps or to use new starting materials have been studied extensively. 1-Amino-2-chloro-4-hydroxyanthraquinone (the intermediate for disperse red dyes) conventionally requires four steps from anthraquinone and four separation (filtration and drying) operations. In recent years an improved process has been proposed that involves three reactions and only two separation operations starting from chlorobenzene (Fig. 2).

Because of their small extinction coefficients anthraquinone dyes have less tinctorial strength than azo dyes; that is the intrinsic disadvantage of

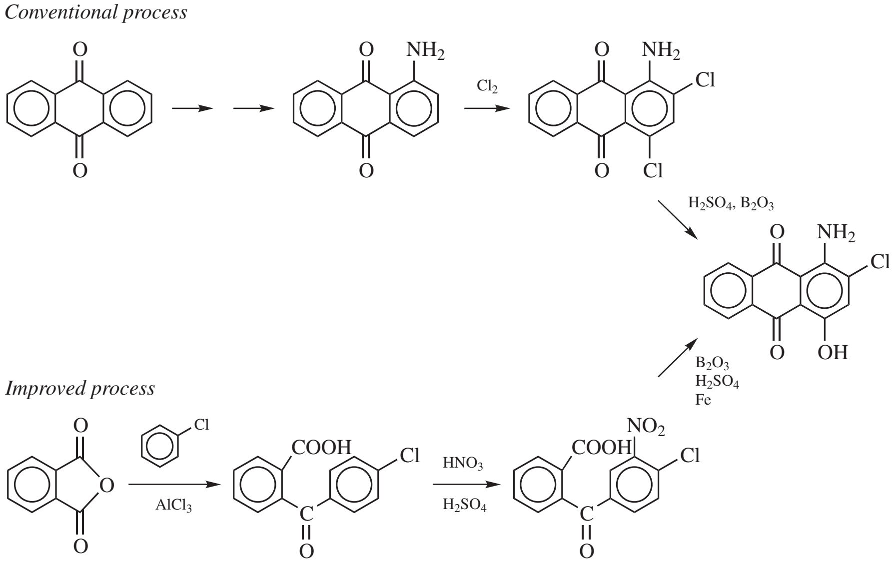
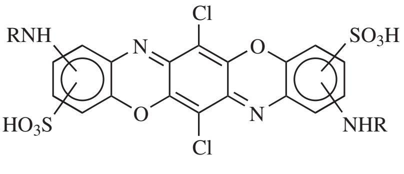


Fig. 2. Manufacturing processes for the dye intermediate 1-amino-2-chloro-4-hydroxyanthraquinone [2478-67-3].

anthraquinones. This fact and the complexity of preparation have made their production costs higher than those of azo dyes (qv). However, the anthraquinone dyes have excellent properties that are not attainable by azo dyes, such as brilliancy of color, fastness, and excellent dyeing properties (leveling and dye bath stability). Thus the anthraquinone dyes have been widely used in the areas where these properties are required. Cotton or polyester–cotton blend fibers for military wear and working wear that require extreme fastness are dyed mainly with anthraquinone vat dyes. Most polyester fabrics for automobile seats are dyed with anthraquinone disperse dyes, since the requirement for lightfastness is extremely high and, simultaneously, bright shades are needed.

World dye manufacturers have already begun to develop new types of dyes that can replace the anthraquinones technically and economically (1). Some successful examples can be found in azo disperse red and blue dyes. Examples are brilliant red [68353-96-6] and CI Disperse Blue 165 [41642-51-7] (CI 11077). They have come close to the level of anthraquinone reds and blues, respectively, in terms of brightness. In the reactive dye area intensive studies have continued to develop triphenodioxazine compounds, eg, (**13**), which are called new blues, to replace anthraquinone blues. In this representation R designates the substituents having reactive groups.



(**13**)

2.2. Method of Synthesis. Anthraquinone dyes are derived from several key compounds called dye intermediates, and the methods for preparing these key intermediates can be divided into two types: (*1*) introduction of substituent(s) onto the anthraquinone nucleus, and (*2*) synthesis of an anthraquinone nucleus having the desired substituents, starting from benzene or naphthalene derivatives (nucleus synthesis). The principal reactions are nitration and sulfonation, which are very important in preparing α-substituted anthraquinones by electrophilic substitution. Nucleus synthesis is important for the production of β-substituted anthraquinones such as 2-methylanthraquinone and 2-chloroanthraquinone. Friedel-Crafts acylation using aluminum chloride is applied for this purpose. Synthesis of quinizarin (1,4-dihydroxyanthraquinone) is also important.

3. Color and Structure

The uv–vis spectrum of anthraquinone shows an absorption maximum at 323 nm ($\epsilon = 4500$) due to a π-π* transition and very weak absorption in the visible range, 405 nm ($\epsilon = 60$) due to a *n*-π* transition. Thus anthraquinone is almost colorless. Introduction of electron-donating substituents causes a bathochromic shift. This is due to the charge-transfer band from the lone pair of amino or hydroxyl groups to the oxygen atom of the carbonyl group. By increasing the electron-donating ability of substituents, the bathochromic shifts are enhanced (Table 1). In the case of the same substituent, the bathochromic shift is larger when the substituent is in the 1-position rather than in the 2-position. The introduction of an electron-withdrawing group has little effect on the absorption maximum of the spectrum.

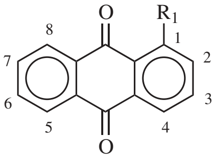
A methylamino group is more effective than a dimethylamino group as an electron donor. This is interpreted in terms of hydrogen-bonding of the substituent with the adjacent carbonyl group that promotes the conjugation of the lone

Table 1. **Spectral Data for Some Monosubstituted Anthraquinones[a] in Methanol**

	1-position		2-position	
Substituent	λ_{max}, nm	ε	λ_{max}, nm	ε
Electron-donating groups				
OCH_3	378	5200	363	3950
OH	402	5500	368	3900
$NHCOCH_3$	400	5600	367	4200
NH_2	475	6300	440	4500
$NHCH_3$	503	7100	462	5700
$N(CH_3)_2$	503	4900	472	5900
Electron-withdrawing groups				
NO_2	325	4300	323	5200
Cl	333	5000	325	3900

[a] Unsubstituted anthraquinone $\lambda_{max} = 323$ nm; ε = 4500.

Table 2. **Spectral Data for Some Disubstituted Anthraquinones in Methanol**



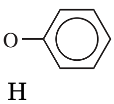
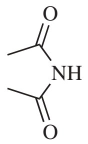
R_1	R_2[a]	λ_{max}, nm	ε
NH_2	H	475	6,500
NH_2	5-NH_2	487	12,600
NH_2	8-NH_2	507	10,000
NH_2	4-NH_2	550, 590	15,850, 15,850
NH_2	4-OH	528, 563	11,670, 9,540
OH	H	402	5,500
OH	5-OH	425	10,000
OH	8-OH	430	10,960
OH	4-OH	470	17,000

[a] Numerical locant indicates substituent position.

pair of electrons of the donor. Also, a sterically hindered dimethylamino group in the 1-position is unable to conjugate, which decreases the extinction coefficient as well.

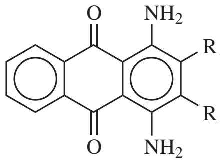
The absorption maximum of a disubstituted anthraquinone greatly depends on the substituents and their positions (Table 2). The 1,4-disubstituted compound shows a remarkable bathochromic shift. The effects of β-substituents on 1,4-diaminoanthraquinones (**14**) are shown in Table 3. Larger bathochromic

Table 3. **Spectral Data for 2- and 3-Substituted 1,4-Diaminoanthraquinones[a] in *N,N*-Dimethylformamide**

R	Monosubstitution (2-) λ_{max}, nm	Disubstitution (2-,3-) λ_{max}, nm
		550, 588
H	553, 594	553, 594
Cl	559, 598	563, 601
SO_3H	562, 603	596, 637
COOH	603	
		666

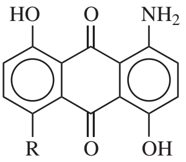
[a] Structure (**14**).

shifts are observed with increasing electron-withdrawing ability of β-substituents.

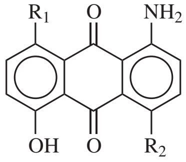


(**14**)

1,4,5,8-Tetrasubstituted anthraquinones give a slightly reddish blue tint to greenish blue color depending on the substituents and their positions, eg, 1,4,5,8-tetraaminoanthraquinone is blue green.



R = OH, slightly reddish blue
R = NH_2, neutral blue

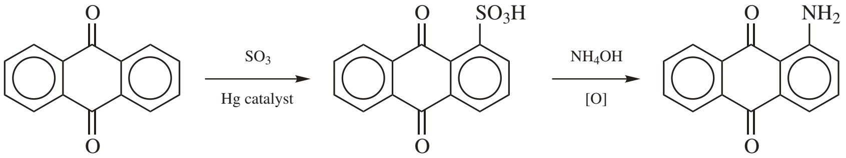


$R_1 = NH_2$; $R_2 = OH$; slightly greenish blue
$R_1 = OH$; $R_2 = NH_2$, greenish blue

In addition to the color and the tinctorial strength, which are very important factors for the molecular design of anthraquinone dyes, affinity for fibers, various kinds of fastness (light, wet, sublimation, nitrogen oxides (NO_x) gas, washing, etc), and application properties (sensitivity for dyeing temperature, pH, etc) must be considered thoroughly as well.

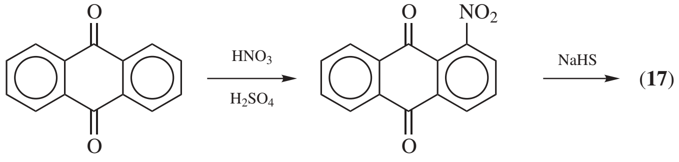
4. Key Intermediates

4.1. 1-Aminoanthraquinone and Related Compounds. 1-Aminoanthraquinone [82-45-1] (**17**) is the most important intermediate for manufacturing acid, reactive, disperse, and vat dyes. It has been manufactured from anthraquinone-1-sulfonic acid [82-49-5] (**16**) by ammonolysis of the sulfo group with aqueous ammonia in the presence of an oxidizing agent such as nitrobenzene-3-sulfonic acid.



(**15**) (**16**) (**17**)

In this process the starting material can only be obtained by mercury-catalyzed sulfonation of anthraquinone [84-65-1] (**15**) with oleum. For improved ecology, the alternative route based on 1-nitroanthraquinone [82-34-8] (18) was established. 1-Nitroanthraquinone is prepared from anthraquinone by nitration in sulfuric acid or organic solvent. 1-Aminoanthraquinone can be prepared from 1-nitroanthraquinone by reduction with sodium sulfide, sodium hydrogen sulfide in water (2), in organic solvent (3), with hydrazine hydrate (4), or by catalytic hydrogenation (5).



(**18**)

Purification is carried out by recrystallization from organic solvent (6) or from sulfuric acid (7). Highly purified product is manufactured by continuous vacuum distillation (8).

One purification method applies the difference in oxidation rate between the leuco forms of the mono- and diaminoanthraquinones. Thus a mixture of 1-aminoanthraquinone and diaminoanthraquinones are first reduced by treating with dithionite in aqueous alkaline solution or by catalytic hydrogenation to convert to the leuco form, ie, corresponding anthrahydroquinones. Then, by subsequent partial oxidation by air, diaminoanthrahydroquinones are oxidized selectively to regenerate the quinoide form, and are separated from water- soluble 1-aminoanthrahydroquinone (9,10).

1-Nitroanthraquinone (**18**) is now the key intermediate for 1-aminoanthraquinone. The classical route from anthraquinone-1-sulfonic acid has become less competitive, because perfect recovery of mercury catalyst is demanded, and this requires a large investment.

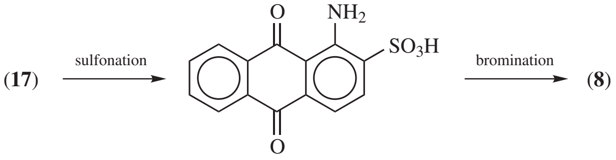
1-Nitroanthraquinone is prepared from anthraquinone by nitration in sulfuric acid (11), or in organic solvent (12). Nitration in nitric acid is dangerous. The mixture of anthraquinone and nitric acid forms a Sprengel mixture (13,14) which may detonate. However, detonation can be prevented by adding an inert third component such as sulfuric acid. Experimental results of the steel-tube detonation tests for the anthraquinone–HNO_3–H_2SO_4 system have been published (13).

The nitration route shows insufficient alpha-selectivity in addition to producing considerable dinitro product. Although a large amount of work has been done to maximize the yield of 1-nitro compound, the best result is less than 80%. Several methods have been developed to remove 2-nitroanthraquinone and dinitroanthraquinones from crude 1-nitroanthraquinone. Purification is carried out, for example, by recrystallization from nitric acid, or from organic solvents (15).

The oxidation of 1-nitronaphthalene by ceric ammonium nitrate has been reported (16). The resulting 1-nitronaphthoquinone condenses with 1,3-butadiene followed by air oxidation under alkaline conditions to form 1-nitroanthraquinone, or 1-aminoanthraquinone is formed directly by an intramolecular redox reaction.

Efforts to raise the alpha-selectivity have been made. Thus nitration of anthraquinone using nitrogen dioxide and ozone has been reported (17).

1-Amino-4-bromoanthraquinone-2-sulfonic acid (bromamine acid) [116-81-4] (8) is the most important intermediate for manufacturing reactive and acid dyes. Bromamine acid is manufactured from 1-aminoanthraquinone-2-sulfonic acid [83-62-5] (**19**) by bromination in aqueous medium (18–20), or in concentrated sulfuric acid (21). 1-Aminoanthraquinone-2-sulfonic acid is prepared from 1-aminoanthraquinone by sulfonation in an inert, high boiling point organic solvent (22), or in oleum with sodium sulfate (23).

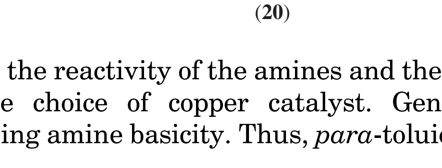


(**19**)

In the first case (22), almost stoichiometric amounts of sulfuric acid or chlorosulfonic acid are used. The amine sulfate or the amine chlorosulfate is, first, formed and heated to about 180 or 130°C, respectively, to rearrange the salt. The introduction of the sulfonic acid group occurs only in the ortho position, and an almost quantitative amount of 1-aminoanthraquinone-2-sulfonic acid is obtained. On the other hand, the use of oleum (23) requires a large excess of SO_3 to complete the reaction, and inevitably produces over-sulfonated compound such as 1-amino-anthraquinone-2,4-disulfonic acid. Addition of sodium sulfate reduces the byproduct to a certain extent. Improved processes have been proposed to make the isolation of the intermediate (19) unnecessary (24,25).

Contamination by water-insoluble reaction by-products such as 1-amino-2,4-dibromoanthraquinone affects the quality of dyestuff significantly. Therefore, several methods for purification have been reported. Examples are extraction of impurities with organic solvent (18), or precipitation of bromamine acid from concentrated (60–85%) sulfuric acid (26).

Many anthraquinone reactive and acid dyes are derived from bromamine acid. The bromine atom is replaced with appropriate amines in the presence of copper catalyst in water or water–alcohol mixtures in the presence of acid binding agents such as alkali metal carbonate, bicarbonate, hydroxide, or acetate (Ullmann condensation reaction).

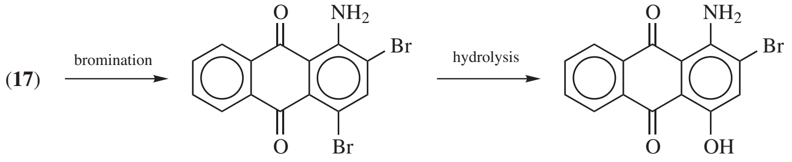


(**20**)

Yields depend on the reactivity of the amines and the choice of reaction conditions, including the choice of copper catalyst. Generally, the reactivity increases with increasing amine basicity. Thus, *para*-toluidine ($\mathrm{p}K_a = 5.1$) reacts four times faster than aniline (p$K_a = 4.7$) (27). Sterically hindered amines such as 3,5-di-amino-2,4,6-trimethylbenzenesulfonic acid react very slowly.

The main by-products of the Ullmann condensation are 1-aminoanthraquinone-2-sulfonic acid and 1-amino-4-hydroxyanthraquinone-2-sulfonic acid. The choice of copper catalyst affects the selectivity of these by-products. Generally, metal copper powder or copper(I) salt catalyst has a greater reactivity than copper(II) salts. However, they are likely to yield the reduced product (1-amino-anthraquinone-2-sulfonic acid). The reaction mechanism has not been established. It is very difficult to clarify which oxidation state of copper functions as catalyst, since this reaction involves fast redox equilibria where anthraquinone derivatives and copper compounds are concerned. Some evidence indicates that the catalyst is probably a copper(I) compound (28,29).

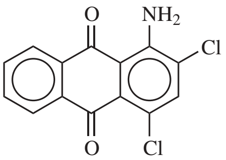
1-Amino-2-bromo-4-hydroxyanthraquinone (bromo pink) [116-82-5] (**22**) is one of the most important intermediates for manufacturing red disperse dyes. It is prepared by dibrominating 1-aminoanthraquinone (**17**) in concentrated sulfuric acid and subsequent hydrolysis in the presence of boric acid. These two reactions are carried out in one pot without isolation of 1-amino-2,4-dibromoanthraquinone [81-49-2] (**21**) (30–32).



(**21**) (**22**)

Furthermore, a method using formaldehyde in the second step (hydrolysis) instead of boric acid has been reported recently (33). 1-Amino-4-hydroxyanthraquinone [116-85-8] is also brominated to form 1-amino-2-bromo-4-hydroxyanthraquinone [116-82-5]. Bromination is carried out in an inert organic solvent such as nitrobenzene (34).

1-Amino-2-chloro-4-hydroxyanthraquinone (chloro pink) [2478-67-3] (**23**) is another important intermediate in red disperse dye manufacture. 1-Amino-2-chloro-4-hydroxyanthraquinone is prepared via a route from chlorobenzene and phthalic anhydride as the raw materials (35) (see Fig. 2). 2-(4′-Chlorobenzoyl)-benzoic acid is nitrated in concentrated sulfuric acid, then reduction of the nitro group, ring closure, and hydrolysis occur simultaneously in concentrated sulfuric acid in the presence of a reducing agent and boric acid. Thus obtained crude chloro pink is purified by selective precipitation from sulfuric acid in order to separate it from by-produced 2-amino-3-chloro-1-hydroxyanthraquinone (**24**) (36).



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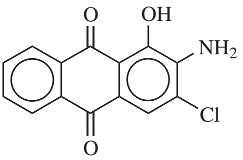
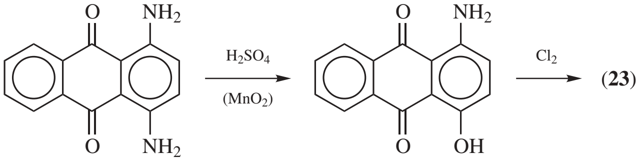


(**24**)

1-Amino-2-chloro-4-hydroxyanthraquinone can be prepared from 1-amino-2,4-dichloroanthraquinone by selective hydrolysis of the chlorine atom in the 4-position in concentrated sulfuric acid in the presence of boric acid in the same manner as bromo pink. However, 1-amino-2,4-dichloroanthraquinone [13432-32-1] cannot be practically obtained by chlorination of 1-aminoanthraquinone in concentrated sulfuric acid. Rather, 1-amino-2,4-dichloroanthraquinone must be prepared by chlorinating 1-aminoanthraquinone in an organic solvent (37), or in thionyl chloride (38), and isolating it.

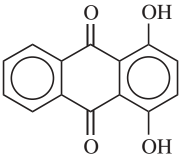
1-Amino-4-hydroxyanthraquinone (**25**) can be used as the starting material for 1-amino-2-chloro-4-hydroxyanthraquinone (**23**). Chlorination is carried out in concentrated sulfuric acid with chlorine gas in the presence of a catalytic amount of $FeCl_3$ (39). 1-Amino-4-hydroxyanthraquinone is prepared by oxidizing 1,4-diaminoanthraquinone in concentrated sulfuric acid with a catalytic amount of manganese dioxide (39).



(**25**)

4.2. 1,4-Dihydroxyanthraquinone.

This anthraquinone, also known as quinizarin [81-64-1] (**26**), is of great importance in manufacturing disperse, acid, and vat dyes. It is manufactured by condensation of phthalic anhydride with 4-chlorophenol [106-48-9] in oleum in the presence of boric acid or boron trifluoride (40,41). Improved processes for reducing waste acid have been reported (42), and yield is around 80% on the basis of 4-chlorophenol.

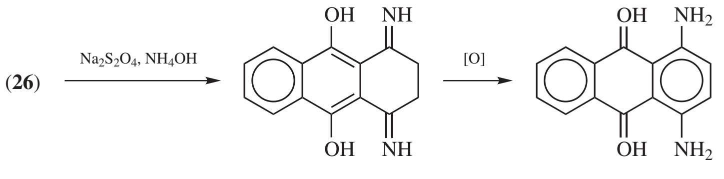


(**26**)

In this reaction, three steps, ie, acylation, cyclization, and replacement of the chlorine atom by the hydroxyl group, take place simultaneously in concentrated sulfuric acid. In the course of cyclization 2,7-dichlorofluoran may be formed as a by-product presumably through the carbonium ion. The addition of boric acid suppresses this pathway and promotes the regular cyclization to form the anthraquinone structure. The stable boric acid ester formed also enables the complete replacement of chlorine atoms by the hydroxyl group. Hydrolysis of the boric acid ester of quinizarin is carried out by heating in dilute sulfuric acid. The purity of quinizarin thus obtained is around 90%. Highly pure product can be obtained by sublimation.

Hydroquinone may also be used in place of 4-chlorophenol. In this case an aluminum chloride–sodium chloride melt is usually employed. However, the yield is not satisfactory (43). It has also been reported that the reaction of hydroquinone with substantially stoichiometric phthalic acid dichloride in the presence of anhydrous aluminum chloride in moderately polar solvents, such as nitrobenzene at around 100°C gives quinizarin (44). The reported yield is 65% after purification by crystallization from toluene.

4.3. 1,4-Diaminoanthraquinone and Related Compounds. Leuco-1,4-diaminoanthraquinone [81-63-0] (leucamine) (**27**) is an important precursor for 1,4 diaminoanthraquinone [128-95-0] (**28**) and is prepared by heating 1,4-dihydroxyanthraquinone (**26**) with sodium dithionite in aqueous ammonia under pressure.



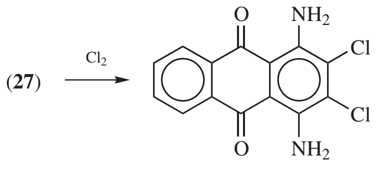
(**27**) (**28**)

1,4-Diaminoanthraquinone is an important intermediate for vat dyes and disperse dyes, and is prepared by oxidizing leuco-1,4-diaminoanthraquinone with nitrobenzene in the presence of piperidine. An improved process has been reported (45).

1,4-Diaminoanthraquinone-2-sulfonic acid [4095-85-6] is a possible precursor of 1,4-diamino-2,3-dicyanoanthraquinone, and is prepared from 1-amino-4-bromoanthraquinone-2-sulfonic acid (**8**) by reaction with liquid ammonia in the presence of copper catalyst (46,47).

Instead of liquid ammonia, aqueous ammonia is also used together with a polar aprotic solvent such as formamide (48). It is also prepared by sulfonating 1,4-diaminoanthraquinone (**28**) with chlorosulfonic acid (49), sulfuric acid, or oleum (50).

1,4-Diamino-2,3-dichloroanthraquinone [81-42-5] (**29**) (CI Disperse Violet 28) is an important compound as an intermediate for CI Disperse Blue 60 and CI Disperse Violet 26, and is prepared by chlorination of leuco-1,4-diaminoanthraquinone (**27**) with chlorine gas or sulfuryl chloride in an inert organic solvent such as nitrobenzene (51,52).



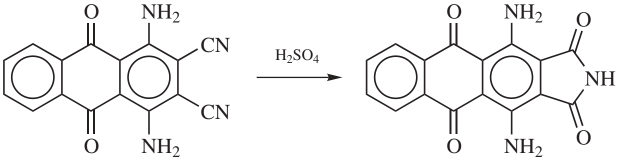
(**29**)

1,4-Diamino-2,3-dicyanoanthraquinone [81-41-4] (**30**) is the key intermediate for manufacturing CI Disperse Blue 60. 1,4-Diamino-2,3-dicyanoanthraquinone is manufactured by reaction of 1,4-diaminoanthraquinone-2,3-disulfonic acid (**36**) with alkali metal cyanide (53). A one-pot process from 1,4-diamino-2,3-dichloroanthraquinone, ie, sulfonation with alkali metal sulfite in the presence of quaternary ammonium compound and subsequent cyanation without isolation of the intermediate, has been proposed (54).

It is also prepared by direct cyanation of 1,4-diamino-2,3-dichloroanthraquinone (**29**) or 1,4-diaminoanthraquinone (**28**) in an aprotic organic solvent. In the latter case, the presence of an ammonium compound and a dehydrogenating agent is necessary (55).

A process from 1,4-diaminoanthraquinone-2-sulfonic acid has also been proposed. In this case, cyanation is preferably carried out in an aqueous medium in the presence of a dehydrogenating agent such as nitrobenzene-3-sulfonic acid, and a quaternary ammonium compound (56). Cyanation in an aprotic solvent such as formamide or 1-methoxypropan-2-ol has also been proposed (57,58). Cyanation of the derivative of 1,4-diaminoanthraquinone in 2-pyrrolidinone has also been proposed. The starting material is prepared by reaction of 1,4-diaminoanthraquinone with boron trifluoride–diethyl ether complex (59).

1,4-Diaminoanthraquinone-2,3-dicarboxyimide [128-81-4] (31) is the intermediate for CI Disperse Blue 60, in which the imide H is replaced by the R group —$CH_2CH_2CH_2OCH_3$. Compound (31) is prepared by hydrolysis of 1,4-diamino-2,3-dicyanoanthraquinone in concentrated sulfuric acid.



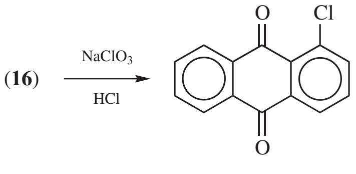
(**30**) (**31**)

4.4. Anthraquinone-1-sulfonic acid and Its Derivatives.

Anthraquinone-1-sulfonic acid [82-49-5] (**16**) has become less competitive than 1-nitroanthraquinone as the intermediate for 1-aminoanthraquinone. However, it still has a great importance as an intermediate for manufacturing vat dyes via 1-chloroanthraquinone.

Anthraquinone-1-sulfonic acid is prepared from anthraquinone by sulfonation with 20% oleum in the presence of mercury catalyst, a Hg(II) salt such as $HgSO_4$ or HgO, at 120°C. Direct sulfonation with the oleum in the absence of mercury catalyst at the same temperature produces the 2-sulfonic acid exclusively. Although the 1-position in anthraquinone is much more reactive than is the 2-position, as predicted by calculations of the localization energy of π-electrons, the formation of 2-isomer, which is not sterically hindered by an adjacent carbonyl group, is thermodynamically favored. Anthraquinone-1-sulfonic acid is isolated as the potassium salt. Thus, after completion of sulfonation, the reaction mixture is charged into a large excess of water, heated, and unreacted anthraquinone is separated by filtration. The potassium salt is precipitated from the filtrate by adding potassium chloride solution, and isolated by filtration. Demercuration of the sulfonation mixture using sulfur compounds such as CH_3CSNH_2 etc, has been proposed (60).

1-Chloroanthraquinone [82-44-0] (**32**) is an intermediate for manufacturing vat dyes such as CI Vat Brown 1. 1-Chloroanthraquinone is prepared by chlorination of anthraquinone-1-sulfonic acid with sodium chlorate in hydrochloric acid at elevated temperature (61). An alternative route from 1-nitroanthraquinone (18) using elemental chlorine at high temperature has been reported (62).



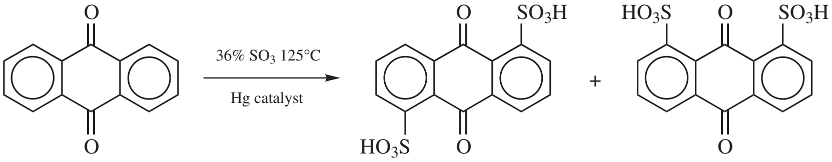
(**32**)

1-Methylaminoanthraquinone [82-38-2] is an important intermediate for manufacturing solvent dyes and acid dyes, and is prepared from anthraquinone-1-sulfonic acid by replacing the SO_3H group with methylamine. An oxidizing agent such as *m*-nitrobenzenesulfonic acid is usually added to oxidize the liberated sulfite. 4-Bromo-1-methylaminoanthraquinone [128-93-8] is a precursor of *N*-methylanthrapyridone and is prepared from 1-methylaminoanthraquinone by bromination (63).

4.5. Anthraquinone-α,α′-disulfonic acids and Related Compounds.

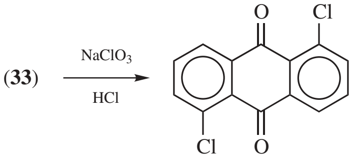
Anthraquinone-α,α′-disulfonic acids and their derivatives are important intermediates for manufacturing disperse blue dyes (via 1,5-, or 1,8-dihydroxyanthraquinone, or 1,5-dichloroanthraquinone) and vat dyes (via 1,5-dichloroanthraquinone).

Anthraquinone-1,5-disulfonic acid [117-14-6] (**33**), and anthraquinone-1, 8-disulfonic acid [82-48-4] (**34**) are produced from anthraquinone by disulfonation in oleum; a higher concentration of SO_3 than that used for 1-sulfonic acid is employed in the presence of mercury catalyst (64,65). After completion of sulfonation, 1,5-disulfonic acid is precipitated by addition of dilute sulfuric acid and separated. After clarification with charcoal, 1,5-disulfonic acid is precipitated as the sodium salt by addition of sodium chloride. The 1,8-disulfonic acid is isolated as the potassium salt from the sulfuric acid mother liquor by addition of potassium chloride solution.



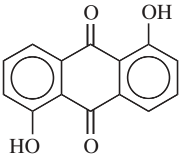
(**33**) (**34**)

1,5-Dichloroanthraquinone[82-46-2] (**35**) is an important intermediate for vat dyes and disperse blue dyes. 1,5-Dichloroanthraquinone is prepared by the reaction of anthraquinone-1,5-disulfonic acid with $NaClO_3$ in hot hydrochloric acid solution. Alternative methods from 1,5-dinitroanthraquinone by reaction of chlorine at high temperature in the presence of phthalic anhydride have been proposed (66).



(**35**)

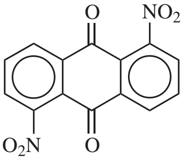
1,5-Dihydroxyanthraquinone (anthrarufin) [117-12-4] (**36**) is an important intermediate for manufacturing disperse blue dyes, eg, CI Disperse Blue 73, and is prepared from anthraquinone-1,5-disulfonic acid by heating with an aqueous suspension of calcium oxide and magnesium chloride under pressure at 200–250°C (67). Alternative methods have been proposed, ie, direct replacement of the NO_2 groups of 1,5-dinitroanthraquinone (68) or the route via 1,5-dimethoxyanthraquinone [6448-90-4] and subsequent hydrolysis (69).



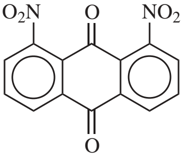
(**36**)

1,8-Dihydroxyanthraquinone (chrysazin) [117-10-2] is prepared in a similar manner to that for anthrarufin.

4.6. α,α′-Dinitroanthraquinones and Related Compounds. 1,5- and 1,8-Dinitroanthraquinone are the key intermediates for manufacturing disperse blue dyes via dinitrodihydroxyanthraquinone and vat dyes via diaminoanthraquinones. 1,5-Dinitroanthraquinone [82-35-9] (**37a**) and 1,8-dinitroanthraquinone [129-39-5] (**37b**) are prepared by nitration of anthraquinone with nitric acid in sulfuric acid. α,β′-Dinitroanthraquinones are also formed in the reaction.



(**37a**)



(**37b**)

1,5-Dinitroanthraquinone and 1,8-dinitroanthraquinone can also be prepared by nitration of anthraquinone in concentrated nitric acid (70). The 1,5-isomer can then be easily separated from the reaction mixture by filtration, since 1,8- or other isomers than 1,5-dinitroanthraquinone are completely dissolved in concentrated nitric acid. However, this process is unsuitable for industrial production for safety reasons; the mixture of dinitroanthraquinone and concentrated nitric acid forms a detonation mixture (71). Addition of sulfuric acid makes it possible to work outside the detonation area.

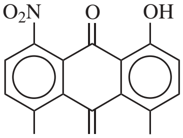
Dinitroanthraquinones are industrially prepared by nitration of anthraquinone in mixed nitric–sulfuric acid at 0–50°C. The reaction mixture is then heated to a temperature slightly higher than the nitration reaction temperature to enrich the content of 1,5-dinitroanthraquinone in solid phase, and then cooled and filtered to obtain the 1,5-dinitroanthraquinone wet cake. Mother liquor is concentrated by distillation of nitric acid and crystallized 1,8-isomer is separated. The filtrate is again distilled, and precipitated β-isomers are filtered off and filtrate is recycled to the nitration step (72–74).

1,5-Diaminoanthraquinone [129-44-2] is prepared from 1,5-dinitroanthraquinone by ammonolysis in organic solvents (75), in aqueous ammonia (76), by catalytic hydrogenation in an organic solvent (77), or by reduction with sodium sulfide. 1,5-Diaminoanthraquinone is also prepared from anthraquinone 1,5-disulfonic acid by ammonolysis in the presence of an oxidizing agent such as *m*-nitrobenzenesulfonic acid (78,79). 1,5-Diaminoanthraquinone is an important intermediate for manufacturing vat dyes such as CI Vat Brown 3 [131-92-0] (**16**) (CI 69015).

1,5-Diphenoxyanthraquinone [82-21-3] is a precursor of 1,5-dihydroxy-4,8-dinitroanthraquinone, and is prepared from 1,5-dinitroanthraquinone and alkali metal phenoxide in phenol (80), or in an inert organic solvent (81). 1,5-Dimethoxyanthraquinone is also a precursor for 1,5-dihydroxy-4,8-dinitroanthraquinone and is prepared from 1,5-dinitroanthraquinone with methanolic alkali metal hydroxide (82,83).

High purity of 1,5-dimethoxyanthraquinone is required for manufacturing disperse blue dyes (CI Disperse Blue 56 (11)). A small amount of unreacted 1,5-dinitroanthraquinone in 1,5-dimethoxyanthraquinone affects the brightness of the dye and makes it much duller. Improved processes have been reported (84,85).

1,5-Dihydroxy-4,8-dinitroanthraquinone [128-91-6] (**38**) is an important dye precursor for CI Disperse Blue 56, and is prepared from 1,5-diphenoxyanthraquinone by hexanitration in sulfuric acid and subsequent hydrolysis with aqueous alkali.

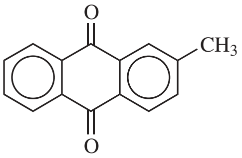


(**38**)

This compound can be converted to 1,5-diamino-4,8-dihydroxyanthraquinone by reduction of nitro groups with sodium sulfide.

1,5-Dinitro-4,8-dihydroxyanthraquinone is also prepared from 1,5-dimethoxyanthraquinone (**48**).

4.7. 2-Methylanthraquinone and Related Compounds. 2-Methylanthraquinone and its derivatives are important as intermediates for manufacturing various kinds of vat dyes and brilliant blue (turqoise blue) disperse dyes. 2-Methylanthraquinone [84-54-8] (**39**) is prepared from phthalic anhydride and toluene via a benzoylbenzoic acid (86).



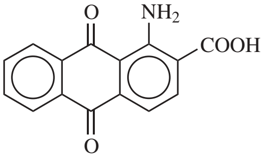
(**39**)

2-Methyl-1-nitroanthraquinone [129-15-7] is an important precursor for 1-nitroanthraquinone-2-carboxylic acid and is prepared by nitration of 2-methylanthraquinone (87). This compound is probably carcinogenic (88).

1-Nitroanthraquinone-2-carboxylic acid [128-67-6] is of great importance as an intermediate for manufacture of vat dyes as well as disperse dyes.

1-Nitroanthraquinone-2-carboxylic acid is conventionally prepared from 2-methyl-1-nitroanthraquinone, by oxidation in sulfuric acid with sodium dichromate. In recent years this process has been faced with the problem of treatment of wastewater containing Cr^{6+}, which cannot be reclaimed, together with a large amount of waste acid. An improved process using HCl and HNO_3 has been proposed to avoid the use of Cr^{6+} (89).

1-Aminoanthraquinone-2-carboxylic acid [82-24-6] (**40**) is also an important intermediate for vat dyes and disperse dyes and is prepared from 1-nitroanthraquinone-2-carboxylic acid by reaction with ammonia.

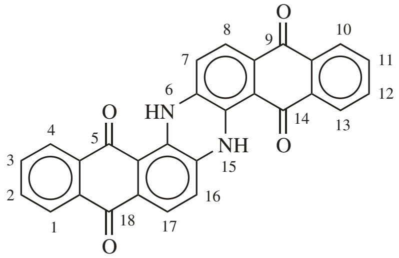


(**40**)

However, the preparation of 1-nitroanthraquinone-2-carboxylic acid has the difficulties mentioned previously. Therefore, new processes for preparing this compound not from the 1-nitro compound but from other precursors have been intensively studied. 1-Aminoanthraquinone derivatives have been proposed for this purpose (90).

4.8. 2-Chloroanthraquinone and Its Derivatives. 2-Chloroanthraquinone and its derivatives are the most important intermediates for vat dyes and high performance organic pigments.

CI Vat Blues 11, 12, and 13 all have the 6, 15-dihydroanthrazinetetrone structure (**6**) as follows. CI Vat Blue 11 (**41**) has Br at positions 7 and 16. CI Vat Blue 13 (**42**) has OH at C-8 and C-17. CI Vat Blue 12 has one OH substituent in an undesignated position. In CI Vat Orange 16 (**43**), position 15 is a carbonyl rather than NH.



(**6**)

2-Chloroanthraquinone [131-09-9] is prepared by Friedel-Crafts reaction of chlorobenzene and phthalic anhydride in the presence of aluminum chloride followed by ring closure in concentrated sulfuric acid (91).

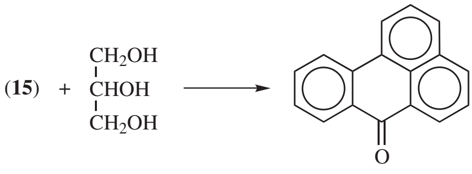
2-Aminoanthraquinone [117-79-3] is prepared by replacement of the chlorine atom in 2-chloroanthraquinone by ammonia (92). This compound has been found to have probable carcinogenicity (93).

2-Amino-3-chloroanthraquinone [84-46-8] is prepared from 2,3-dichloroanthraquinone by partial chlorine replacement by a NH_2 group. 2,3-Dichloroanthraquinone [84-45-7] is prepared by Friedel-Crafts reaction of phthalic anhydride and 1,2-dichlorobenzene followed by ring closure of the resultant benzoylbenzoic acid in sulfuric acid (94).

2-Amino-3-bromoanthraquinone [6337-00-4] is prepared from 2-aminoanthraquinone by bromination in an organic solvent or in sulfuric acid (95).

2-Amino-3-hydroxyanthraquinone [117-77-1] is prepared by heating 5-benzoylbenzoxazolone-2′-carboxylic acid in sulfuric acid (96). This compound is an intermediate for CI Vat Red 10.

4.9. Benzanthrone and Related Compounds. Benzanthrone [82-05-3] (**44**) is prepared by the reaction of anthraquinone (**15**) with glycerol, sulfuric acid, and a reducing agent such as iron.

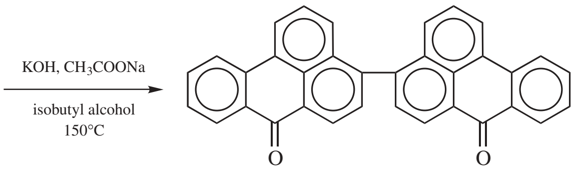


(**44**)

Benzanthrone is an important intermediate for manufacturing vat dyes. Examples are CI Vat Green 1 [128-58-5] (138) via 4,4′-dibenzanthronyl (**45**), CI Vat Blue 20 [116-71-2] (135) via direct KOH−NaOH fusion of benzanthrone, CI Vat Green 3 [3271-76-9] (142), CI Vat Green 5 [1328-37-6], and CI Vat Black 25 [4395-53-3] via 3,9-dibromobenzanthrone [81-98-1].

4,4′-Dibenzanthronyl [116-90-5] (**45**) is a precursor of violanthrone dyes and is prepared from an alcoholic alkali melt of benzanthrone.

(**44**)

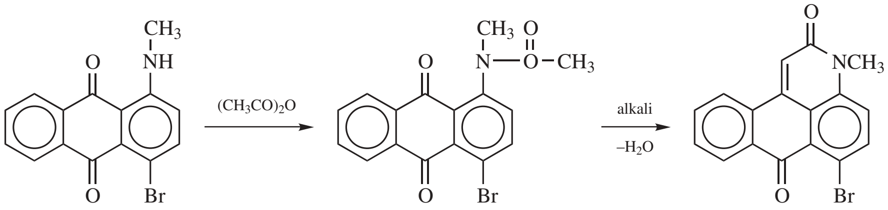


(**45**)

3-Bromobenzanthrone [81-96-9] is prepared from benzanthrone by bromination in hydrochloric acid or in sulfuric acid or in an organic solvent such as nitrobenzene. An improved process has been cited (97). 3,9-Dibromobenzanthrone [81-98-1] is prepared from benzanthrone by bromination in chlorosulfonic acid, concentrated sulfuric acid, or an organic solvent such as nitrobenzene.

4.10. *N*-Methylanthrapyridone and Its Derivatives.

6-Bromo-3-methylanthrapyridone [81-85-6] (**47**) is an important intermediate for manufacturing dyes soluble in organic solvents. These solvent dyes are prepared by replacing the bromine atom with various kinds of aromatic amines. 6-Bromo-3-methylanthrapyridone is prepared from 1-methylamino-4-bromoanthraquinone (**46**) by acetylation with acetic anhydride followed by ring closure in alkali. The starting material of this route is anthraquinone-1-sulfonic acid (**16**).



(**46**) (**47**)

An alternative route from 1-aminoanthraquinone (**17**) has been proposed. Methylation is preferably carried out using dimethyl sulfate or methyl iodide in an organic solvent in the presence of alkali metal hydroxide and a catalytic amount of quaternary ammonium compound (98).

5. Reactive Dyes

Most of the anthraquinone reactive dyes are derived from bromamine acid. These dyes give a bright blue shade and excellent lightfastness. A great number of reactive groups have been proposed; typical examples include sulfatoethylsulfone, dichlorotriazine, monochlorotriazine, monofluorotriazine, and other heterocyclic groups.

5.1. Reactive Sulfatoethylsulfonyl Groups.

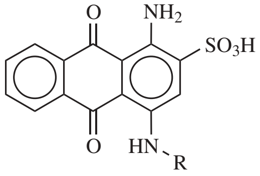
CI Reactive Blue 19 [2580-78-1] (**9**) (CI 61200) is most widely used for dyeing cellulose fibers in exhaustion dyeing, and it gives a brilliant reddish blue shade and excellent lightfastness.

CI Reactive Blue 19 (**9**) is prepared by the reaction of bromamine acid (**8**) with *m*-aminophenyl-β-hydroxyethylsulfone [5246-57-1] in water in the presence of an acid-binding agent such as sodium bicarbonate and a copper catalyst (Ullmann condensation reaction) and subsequent esterification to form the sulfuric ester.

The conventional esterification process requires a large excess of sulfuric acid or oleum; improved processes which minimize the acid wastewater or inorganic salt have been proposed (99–101). One example is esterification of 1-amino-4-[3-(β-hydroxyethylsulfonyl)phenylamino] anthraquinone-2-sulfonic acid [39582-26-8] in an organic solvent containing tertiary amines with a stoichiometric amount of sulfuric acid or sulfamic acid (99). A method in a machine operating with a kneading action using a small excess amount of sulfuric acid or oleum has also been proposed (100). In order to improve the solubility in water or aqueous alkaline solution, a dye composition of CI Reactive Blue 19 (**9**) with its para-isomer, ie, 1-amino-4-[4-(β-sulfatoethylsulfonyl)phenylamino]-anthraquinone-2-sulfonic acid, disodium salt [16102-99-1] has been proposed (102). Another example of a dye with a sulfatoethylsulfonyl group is CI Reactive Blue 27 [20640-71-5] (103).

5.2. Monochloro- or Dichlorotriazine Groups.

Examples of commercial importance are CI Reactive Blue 2 [12236-82-7] (**48**) (CI 61211), CI Reactive Blue 5 [16823-51-1] (**49**) (CI 61205:1), reddish brilliant blue [72927-99-2] (**50**) CI Reactive Blue 4 [13324-20-4] (**51**) (CI 61205). The substituent having the reactive group replaces the Br of (**8**) and the dyes can be represented as follows.



(**48**)–(**54**)

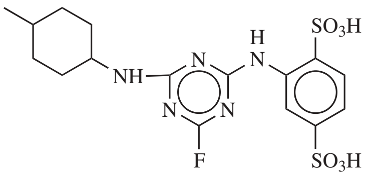
The use of dyes having dichlorotriazine groups is rather limited because the reactivity of this group is so high that the stability of the dyed fiber as well as that of dyestuff itself is not satisfactory.

5.3. Dyes with Other Heterocyclic Reactive Groups.

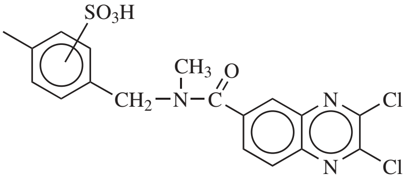
Some heterocyclic reactive components have been developed. Other examples of the dyes of commercial importance are brilliant blue [88318-06-3] (**52**) (monofluorotriazine), blue [83399-87-5] [104601-66-3], (**53**) (dichloroquinoxaline), and brilliant blue [64387-69-5] (**54**) (difluorochloropyrimidine). The R components are shown in Figure 3 for (**52**–**54**).

Reactive green dyes are obtained by combination of a blue chromophore (a bromamine acid derivative) and a yellow chromophore with a triazinyl group. Green [70210-47-8] (104) is an example. The yellow chromophore of this dye was invented by ICI for dichlorotriazine dyes and exhibits good lightfastness and chlorine resistance.

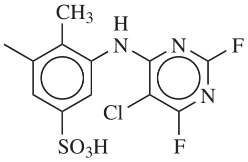
In recent years attempts to replace anthraquinone blue reactive dyes by derivatives of triphenodioxazine chromophores have been successful to a certain extent (105). The triphenodioxazine chromophore has an intrinsically brighter shade and much greater tinctorial strength than anthraquinones. Examples



(**52**)



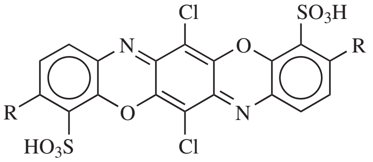
(**53**)



(**54**)

Fig. 3. R groups having reactive heterocyclic groups attached to (**8**) through NH.

are CI Reactive Blue 198 (**55**) (105) and CI Reactive Blue 204 (**56**) (105) in which R is a substituted alkylamino group having a reactive group. In (55) the reactive group is chlorotriazine, in (**56**) it is fluorotriazine.



(**55**), (**56**)

6. Disperse Dyes

Disperse dyes are water-insoluble, aqueous dispersed materials that are used for dyeing hydrophobic synthetic fibers, including polyester, acetate, and polyamide.

In 1923, the first disperse dye was developed for dyeing cellulose acetate fibers. However, in recent years the most important application of disperse dyes has been to dye polyester fibers. Accompanied by the rapid growth of polyester fibers after World War II, disperse dyes have currently achieved the largest production among all dye classes in terms of quantity (106).

By introducing amino, hydroxy, or methyl groups onto the anthraquinone moiety as the principal auxochromes, dyes that have yellow through greenish blue shades are obtained. Among these dyes many that have brilliant red, violet, blue, and greenish blue shades have great industrial importance in view of their affinity for polyester or cellulose acetate fibers and lightfastness and sublimation resistance. On the contrary, yellow or orange dyes are not satisfactory because of the rather simple molecular structure. Therefore these shades are obtained from other chromophores.

On the basis of the kind and the position of their substituents and their color range, the anthraquinoid disperse dyes may be classified as follows:

Color range	Chemical description
red	1-amino-4-hydroxyanthraquinones
blue, greenish blue	1,4,5,8-substituted anthraquinones
greenish blue	1,4-diaminoanthraquinone-2,3-dicarboxyimides
violet, blue	1,4-diaminoanthraquinone derivatives
violet, blue	*N*-substituted 1-amino-4-hydroxyanthraquinones

6.1. 1-Amino-4-hydroxyanthraquinone Derivatives. These compounds in general have bright red shades, good lightfastness, and good affinity for polyester fibers. CI Disperse Red 60 [17418-58-5] (**57**) (CI 60756) is the most typical red dye for polyester fibers. It is widely used for mainly pale and medium shades and for exhaustion dyeing, and exhibits good lightfastness and affinity. It is manufactured by reaction of 1-amino-2-halo(Cl,Br)-4-hydroxyanthraquinone with potassium phenoxide in phenol as the solvent (Fig. 4). Improved methods for reducing the amount of phenol by employing an inert organic solvent such as dimethyl sulfoxide (107), sulfolane (108), or water in the presence of a phase-transfer catalyst (109) have been reported.

1-Amino-2-alkoxy-4-hydroxyanthraquinones have generally brighter and yellower shades than the 2-phenoxy type, and have better lightfastness. Some examples are Disperse Red 55, Disperse Red 91, Disperse Red 92 (110), and Disperse Red 127 (110). These dyes have good sublimation fastness as well.

1-Amino-2-alkoxy-4-hydroxyanthraquinones are prepared by reaction of 1-amino-2-phenoxy-4-hydroxyanthraquinone with the corresponding alcohols (Fig. 5). Improved methods, using 1-amino-2-halo-4-hydroxyanthraquinone as a starting material, have been reported. Thus, 1-amino-2-chloro-4-hydroxyanthraquinone reacts with the alcohol in an inert organic solvent such as chlorobenzene in the presence of an acid binding agent, phenol, and a phase-transfer catalyst (111). For the dyes (**59a**, **b**) and 1-amino-2-(2-hydroxyethoxy)-4-hydroxyanthraquinone is first prepared by the method just described, and then reacts with phenyl or ethyl carbonate (112).

1-Amino-2-(substituted phenoxy)-4-hydroxyanthraquinones, that is (57) with substituents on the phenyl group, have also been developed to improve sublimation fastness.

6.2. 1,4-Diaminoanthraquinone-2,3-dicarboxyimide Derivatives. These dyes have a bright turquoise blue shade and excellent lightfastness and good sublimation fastness. Commercially important examples are CI Disperse Blue 60 [12217-80-0] (**60**) (CI 61104) (113), and CI Disperse Blue 87 [12222-85-4] (114,115).

CI Disperse Blue 60 is prepared by alkylating 1,4-diaminoanthraquinone-2,3-dicarboxyimide [128-81-4] (**31**) with methoxypropylamine in water (116–118)

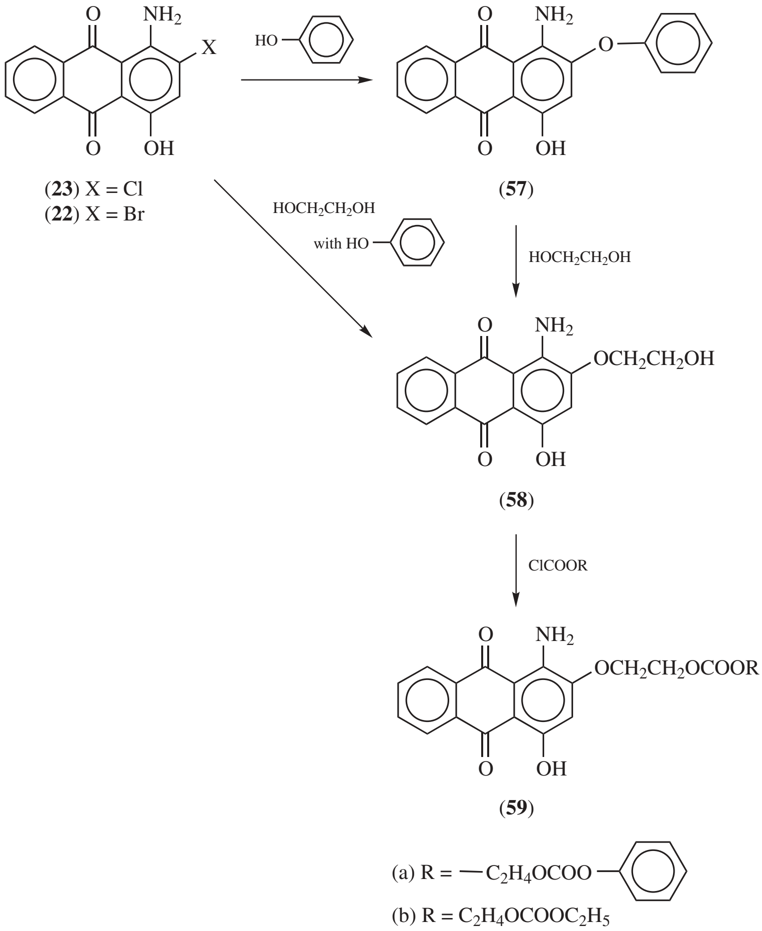
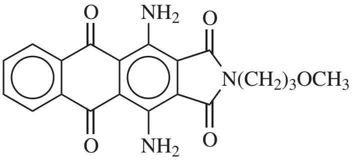


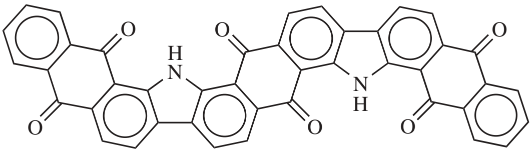
Fig. 4. Synthesis of 1-amino-4-hydroxyanthraquinones with alkoxy substituents in the 2-position.

with or without organic solvent.

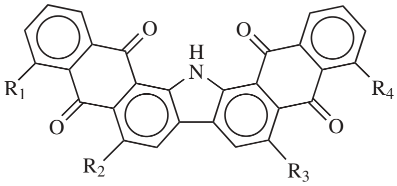


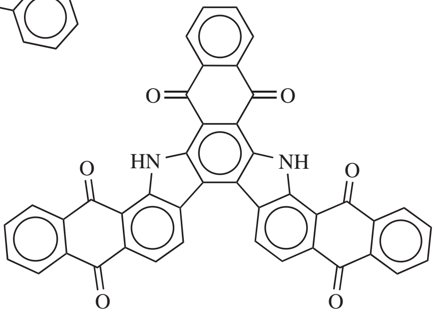
(**60**)

CI Disperse Blue 60 is often used as a mixture with slightly different derivatives (116), that is, the methyl group of (**60**) may be replaced by ethyl, propyl, or $CH_2CH_2OCH_3$.

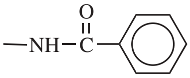


(**75**)

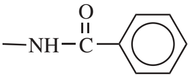




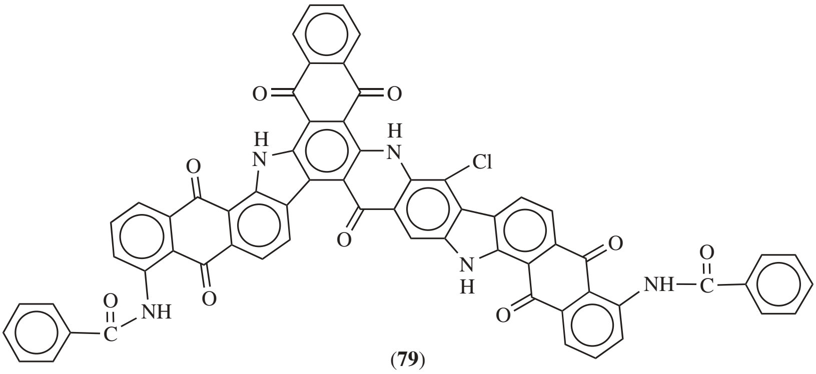
(**77**)

(**76**) R_2, R_3 = H; R_1, R_4 = 

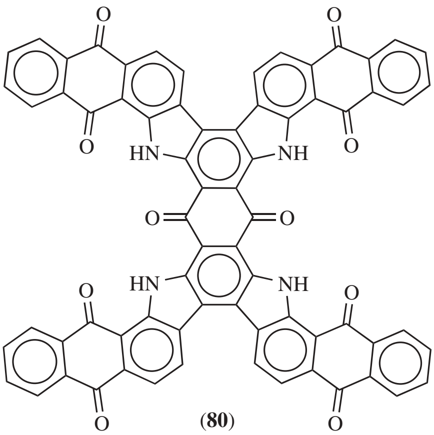
$-NH-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$

(**78**) R_2, R_4 =  ; R_1, R_3 = H

$-NH-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$



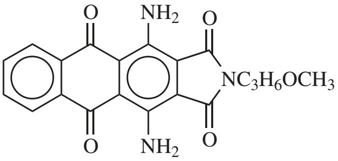
(**79**)



(**80**)

Fig. 5. Anthrimidocarbazole vat dyes.

CI Disperse Blue 87 (**61**) and related dyestuffs are prepared by the reaction of 1-amino-4-nitroanthraquinone-2-carboxylic acid amide with cyanide in water (119).



(**61**)

1-Amino-4-nitroanthraquinone-2-carboxylic acid amide is prepared from 1-nitroanthraquinone-2-carboxylic acid. An improved process has been proposed (120).

1,4-Diaminoanthraquinone-2-carboxylic acid alkylamide is also used as a starting material. In this case, a dehydrogenating agent such as air is necessary (121).

CI Disperse Blue 87 (**59**) and related dyestuffs are also prepared from 1-oxo-3-imino-4,7-diamino-5,6-phthaloylisoindoline [13418-50-3] by alkylation with corresponding alkyl halides (122), sulfonic esters (123), or alkyl amines (124), ie, X of RX = halogen, *p*-toluenesulfonyloxy, or NH_2.

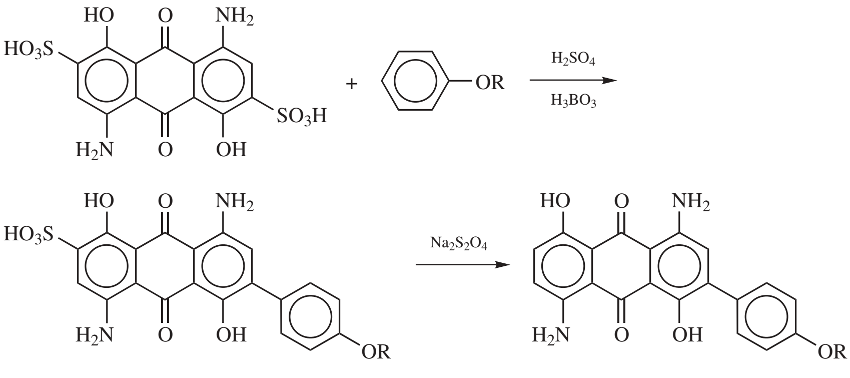
1-Oxo-3-imino-4,7-diamino-5,6-phthaloylisoindoline is prepared by hydrolysis of 1,4-diamino-2,3-dicyanoanthraquinone (**30**) in alcoholic alkaline conditions (125).

6.3. 1,4,5,8-Substituted Anthraquinones. Commercially important blue disperse dyes are derived from 1,4,5,8-substituted anthraquinones. Among them, diaminodihydroxyanthraquinone derivatives are most important in view of their shades and affinity. Representative examples are CI Disperse Blue 56 [31810-89-6] (11) (CI 63285) (126), and CI Disperse Blue 73 (**62**) (115). Introduction of a halogen atom ortho to the amino group improves affinity and lightfastness.

CI Disperse Blue 56 is the most important blue dye for polyester fibers because it has a brilliant shade, excellent lightfastness, and good leveling properties. Disperse Blue 56 is manufactured from 1,5-dihydroxy-4,8-dinitroanthraquinone (**38**).

Conventional 1,5-dichloroanthraquinone has also been used as a starting material. A route via 1,5-diaminoanthraquinone has also been proposed (127); treatment of this compound with Br_2 in H_2SO_4 and H_3BO_3 gives (**11**).

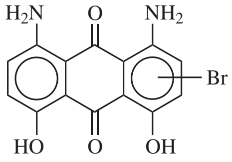
CI Disperse Blue 73 [12222-75-2] (CI 63265) is an example of a dye that was developed to improve sublimation fastness for special use, eg, thermosol dyeing or printing. This dye also has a bright shade, excellent lightfastness and good leveling properties. CI Disperse Blue 73 (**62**) is prepared as follows, where R = H or CH_3.



(**62**)

The starting material is an acid dye, ie, CI Acid Blue 45 which is prepared from 1,5-dihydroxyanthraquinone by sulfonation followed by nitration and then reduction.

CI Disperse Blue 81 [12222-79-6] (**63**) (CI 63603) is a 1,8-diamino-4,5-dihydroxyanthraquinone derivative. Its shade is greenish blue and much duller than CI Disperse Blue 56. Bromo-derivatives of pure 1,8-diamino-4,5-dihydroxyanthraquinone have a bright greenish blue shade, but CI Disperse Blue 81 generally contains other isomers derived mainly from the starting material 1,8-dinitroanthraquinone, which affect the shade significantly.

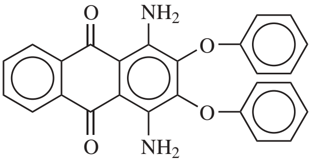


(**63**)

1-Arylamino-8-nitro-4,5-dihydroxyanthraquinones are of importance because of their greenish blue shade and good fastness to light and sublimation. A representative example is 1-anilino-4,5-dihydroxy-8-nitroanthraquinone [20241-76-3] (128). It is prepared by the reaction of 1,8-dinitro-4,5-dihydroxyanthraquinone with aniline.

6.4. 1,4-Diaminoanthraquinones (Except Turquoise Blue Dyes). This dye class generally gives reddish violet, violet, and reddish blue shades. Dyes with such neutral tints are relatively less important today, since dyeing of polyester fibers with the blend of three primary colors has become popular. However, some dyes that have excellent affinity, lightfastness, and sublimation resistance remain commercially important. Examples are CI Disperse Violet 28 [81-42-5] (CI 61102) (**29**), and CI Disperse Violet 26 [6408-72-6] (CI 62025) (**64**). CI Disperse Violet 28 is obtained by introducing chlorine atoms in the 2,3-position of 1,4-diaminoanthraquinone. The introduction of chlorine leads to a bathrochomic shift and improves lightfastness considerably.

CI Disperse Violet 26 is prepared by the reaction of 1,4-diamino-2,3-dichloroanthraquinone (CI Disperse Violet 28 with potassium phenoxide in phenol as a solvent at high temperature. Introduction of phenoxy groups into the 2,3-position shifts the shade to bright, reddish violet and improves the lightfastness and sublimation resistance.



(**64**)

6.5. *N*-Substituted-1-Amino-4-hydroxyanthraquinones.

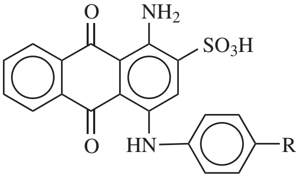
These dyes show good affinity and lightfastness and give violet to blue shades. However, the sublimation fastness is in general not satisfactory. An example is CI Disperse Blue 72 [81-48-1] (CI 60725), prepared from leucoquinizarin and *p*-toluidine.

7. Acid Dyes

Acid dyes are used for dyeing wool, synthetic polyamides, and silk in aqueous media. Anthraquinone acid dyes give brilliant reds, violets, blues, and greens and exhibit excellent lightfastness. Because of their relatively high cost, they are used to dye high grade textiles in pale and moderate shades. Various kinds of anthraquinone acid dyes have been developed so far mainly by IG-Farbenindustrie in Germany applying chemical reactions that were studied in developing vat dyes. However, the number of commercial products has declined because of poor properties or unavailable raw materials. Anthraquinone acid dyes may be classified into two groups: bromamine acid derivatives and quinizarin derivatives.

7.1. Bromamine Acid Derivatives.

Acid dyes derived from bromamine acid (**8**) are important because they give bright blue shades with excellent lightfastness that are not obtainable with azo dyes. Among the bromamine acid derivatives CI Acid Blue 25 [2786-71-2] (**65**) (CI 62055) (129) and CI Acid Blue 40 [6424-85-7] (**66**) (CI 62125) (129) are the first acid dyes, invented in 1913. These dyes are obtained from bromamine acid by reaction with aniline and *p*-aminoacetoanilide respectively. They show good leveling properties in acidic media. However, the wetfastness is not so good.

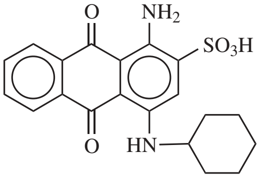


(**65**), $R = H$
(**66**), $R = NHCOCH_3$

Dyes with better wetfastness and better affinity in neutral or weakly acid bath have been developed by introducing more hydrophobic amines. Examples are CI Acid Blue 129 [6397-02-0] (CI 62058), CI Acid Blue 126 [72152-61-5] (130), and CI Acid Blue 230 [12269-82-8] (CI 62073). However, uniform leveling cannot be obtained with these dyes.

Linking of two dye molecules is another method for improving wetfastness. An example is CI Acid Blue 127:1 [12237-86-4] (130), which is obtained by condensing two molecules of CI Acid Blue 25 (118) with formaldehyde.

The shade may be varied by choosing amines. For aromatic amines, the steric effect of substituents in the ortho position reduces the conjugation of the anilino group with the anthraquinone moiety, and the result is a hypsochromic shift and brighter shade. Thus CI Acid Blue 129 has a more reddish and brighter shade than CI Acid Blue 25. Cycloalkylamines have a similar effect on the shade. CI Acid Blue 62 [5617-28-7] (**67**) (CI 62045) is an example.

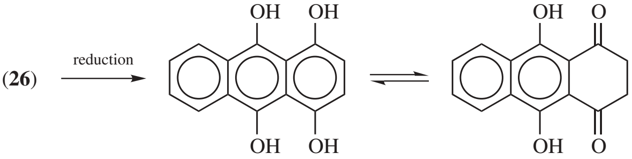


(**67**)

CI Acid Blue 40 (**66**) has a greener and somewhat duller shade than the parent dye (ie, CI Acid Blue 25) (**65**), which is considered to be due to the electronic effect of the *para*-acetylamino group.

In recent years excellent lightfastness and leveling properties have been required for application to nylon carpet.

7.2. Quinizarin Derivatives. Acid dyes derived from the reaction products of quinizarin with aromatic or aliphatic amines are important commercially and predominant in number. They are prepared from leucoquinizarin (**68a**), the reduced form of quinizarin (**26**). The dominant structure of leucoquinizarin is the 2,3-dihydrotautomer (**68b**) (132).



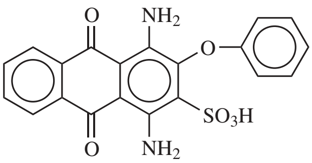
(**68a**) (**68b**)

Alkylamines react with leucoquinizarin in a stepwise manner to give 1-alkylamino-4-hydroxyanthraquinone, and 1,4-dialkylamino derivatives after air oxidation. Aromatic amines react similarly in the presence of boric acid as a catalyst. The complex formed causes the less nucleophilic aromatic amines to attack at the 1-, and 4-positions.

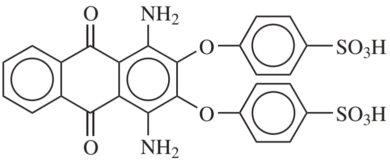
CI Acid Violet 43 [4430-18-6] (**2**) (CI 60730) is one of the first acid dyes, invented in 1894. This dye exhibits good leveling and is available from leucoquinizarin by reaction with *p*-toluidine in the presence of boric acid, followed by oxidation and subsequent sulfonation (133).

CI Acid Green 25 [4403-90-1] (**3**) (CI 61570) was also invented in 1894. This dye shows improved wetfastness, and is prepared from leucoquinizarin by reaction with 2 moles of *p*-toluidine in a similar manner to the preparation of CI Acid Violet 43 (134). Wetfastness and leveling properties may be altered by choosing the substituents of arylamines. The introduction of alkyl groups into aromatic amines improves the wetfastness and affinity in neutral or weekly acid baths. Examples are CI Acid Blue 80 [4474-24-27] (CI 61585) and CI Acid Green 27 [6408-57-7] (CI 61580). Acid Green 27's structure is similar to that of compound (**3**) where CH_3 is replaced by C_4H_9.

1,4-Diamino-2,3-disubstituted anthraquinones are also used as acid dyes. Examples are CI Acid Violet 41 [6408-71-5] (**69**) (CI 62020), and CI Acid Violet 42 [6408-73-7] (**70**) (CI 62026). They are prepared from quinizarin (**26**) through the intermediacy of leucamine (**27**) and 1,4-diamino-2,3-dichloroanthraquinone (**29**) (133).



(**69**)



(**70**)

8. Vat Dyes

Anthraquinone vat dyes have been used to dye cotton and other cellulose fibers for many decades. Despite their high cost, relatively muted colors, and difficulty in application, anthraquinone vat dyes still form one of the most important dye classes of synthetic dyes because of their all-around superior fastness.

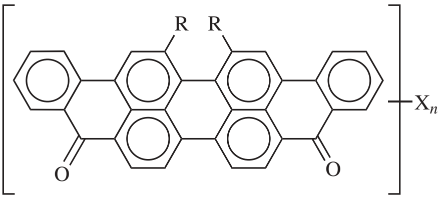
Anthraquinone vat dyes are water-insoluble dyes. They are converted to leuco compounds (anthrahydroquinones) by reducing agents such as sodium hydrosulfite in alkaline conditions. These water-soluble leuco compounds have an affinity to cellulose fibers and penetrate them. After reoxidation by means of air or other oxidizing agents, the dye becomes water-insoluble again and fixes firmly on the fiber.

The anthraquinone vat dyes can be classified into several groups on the basis of their chemical structures: (*1*) benzanthrone dyes, (*2*) indanthrones, (*3*) anthrimides, (*4*) anthrimidocarbazoles, (*5*) acylaminoanthraquinones, (*6*) anthraquinoneazoles, (*7*) anthraquinone acridones, (*8*) anthrapyrimidines, and (*9*) highly condensed ring systems. Available dyes have been known for many decades, and very few new dyes have been commercialized since the 1970s. Recently, research and development efforts have focused on improved manufacturing of traditional vat dyes.

8.1. Benzanthrone Dyes.

Vat dyes derived from benzanthrone may be divided into two groups: violanthrones and isoviolanthrones, dyes that have the perylene ring in their molecular structure; and benzanthrone pyrazolanthrones

Table 4. **Commercially Important Violanthrone Dyes**

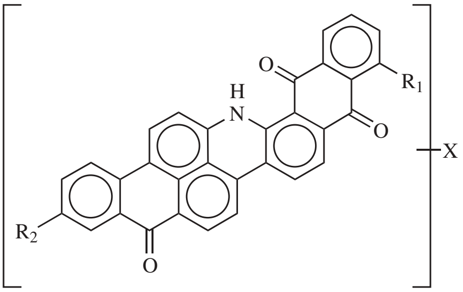


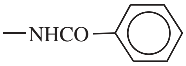
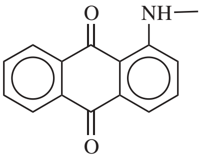
CI Vat name	CAS Registry number	CI number	R	X_n
Blue 20	[116-71-2]	59800	H	H
Blue 18	[1324-54-5]	59815	H	Cl_3
Blue 19	[1328-18-3]	59805	H	Br
Green 1	[128-58-5]	59825	OCH_3	H
Green 2	[25704-81-8]	59830	OCH_3	Br_2

and benzanthrone acridones, the peri ring closure products of 3-anthraquinonylamino-benzanthrone.

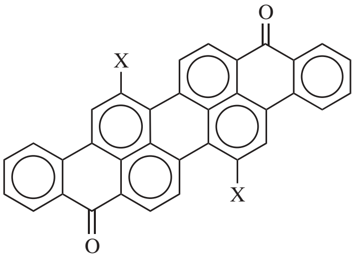
Violanthrone and Isoviolanthrone Dyes. Violanthrone dyes cover a wide range of shades from reddish blue to green and grey. Examples of dyes that have industrial importance appear in Table 4.

Table 5. **Benzanthrone Acridone Vat Dyes**



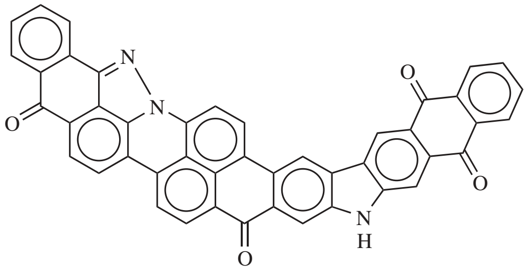
CI Vat name	CAS Registry number	CI number	R_1	R_2	X
Green 3	[3271-76-9]	69500	H	H	H
Green 5	[1328-37-6]	69520		H	Cl
Black 25	[4395-53-3]	69525	H		H

Isoviolanthrones that are currently produced include: CI Vat Violet 1 [1324-55-6] (CI 60010) (**71**) X = Cl, CI Vat Violet 9 [1324-17-0] (CI 60005) (**71**) X = Br, and CI Vat Blue 26 [4430-55-1] (CI 60015) (**71**) X = OCH_3.



(**71**)

Benzanthrone Pyrazolanthrones and Benzanthrone Acridones. Benzanthrone pyrazolanthrones give from navy blue to gray shades and have good fastness. However, the only example of industrial use is CI Vat Black 8 [2278-50-4] (**72**) (CI 71000). CI Vat Blue 25 [6247-39-8] (CI 70500) has the basic structure of this dye class, but it is not produced today.

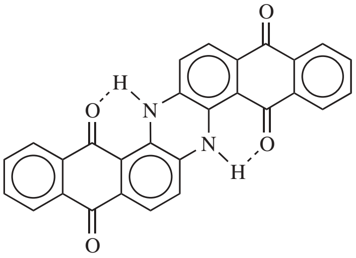


(**72**)

Benzanthrone acridones play an important role in vat dyes, since they give from dark green to olive green shade and have a high color value and excellent fastness. Examples are given in Table 5.

CI Vat Green 3 is prepared from 3-bromobenzanthrone and 1-aminoanthraquinone. CI Vat Black 25 is prepared from dibromobenzanthrone by a similar route. This dye is known as Indanthrene Olive T.

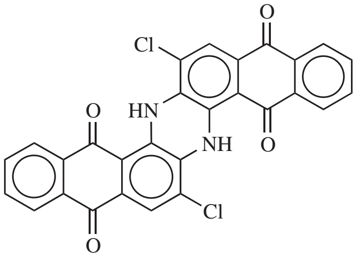
8.2. Indanthrones. Indanthrone blue (CI Vat Blue 4) [81-77-6] (**6**) (CI 69800) is the first invented anthraquinone vat dye, and has been extensively used as the most important vat dye for many decades because of its bright color as well as excellent affinity and fastness. These advantages are considered to be due to the stable structure attained by the intramolecular hydrogen bonding (**73**).



(**73**)

The only drawback of this dye is poor chlorine-fastness, which is considered to be due to the oxidation by chlorine to form a yellowish green azine.

The post-halogenation of indanthrone improves its chlorine resistance to some extent and gives dyes of slightly greener shade. Examples are CI Vat Blue 6 [130-20-1] (**74**) (CI 69825) and CI Vat Blue 14 [1324-27-2] (CI 69810) in which the position of the Cl is not indicated.



(**74**)

CI Vat Blue 4 (**6**) is prepared from 2-aminoanthraquinone by potash fusion in the presence of an oxidizing agent such as sodium nitrite or air. An alternative method by dimerization of 1-aminoanthraquinone (**17**) by using such solvents as dimethyl sulfoxide or tetramethylurea has been reported, and improved methods for this reaction have been cited (135–138). These methods are considered to be advantageous in terms of the yield as well as the availability of starting compounds.

Chlorination of indanthrone in sulfuric acid by passing through chlorine gas with addition of a small amount of manganese dioxide affords CI Vat Blue 14 as well as CI Vat Blue 6.

8.3. Anthrimides.

Despite the facts that anthrimides have excellent leveling properties and cover a wide range of colors from yellow to black, they have little commercial importance because of their duller shades and lower tinctorial strength. However, the anthrimides are important intermediates for manufacturing anthrimidocarbazoles.

8.4. Anthrimidocarbazoles.

Anthrimidocarbazoles cover a wide range of colors (yellow, orange, reddish brown, brown, and green) and have excellent leveling properties. Examples of commercial importance are CI Vat Orange 11 [2172-33-0] (**75**) (CI 70805), CI Vat Orange 15 [2379-78-4] (**76**) (CI 69025), CI Vat Brown 1 [2475-33-4] (**77**) (CI 70800), CI Vat Brown 3 [131-92-0] (**78**) (CI

69105), and CI Vat Brown 55 [4465-47-8] (**79**) (CI 70905). CI Vat Green 8 [14999-97-4] (**80**) (CI 71050) is generally called Indanthrene Khaki GG and has great significance (Fig. 5).

CI Vat Orange 15 is prepared by the reaction of 1-amino-5-benzoylamino-anthraquinone and 1-benzoylamino-5-chloroanthraquinone [117-05-5] followed by ring closure.

CI Vat Brown 1 is prepared from 1,1′:4,1″-trianthrimide(=1,4-bis-(1-anthraquinonylamino)anthraquinone [116-76-7] in aluminum chloride–pyridine melts, followed by work up (by adding to sodium hydroxide solution) and oxidative cleanup (with sodium hypochlorite). 1,1′:4,1″-Trianthrimide is prepared by the condensation of 1,4-diaminoanthraquinone with two moles of 1-chloroanthraquinone at elevated temperature in a high boiling point organic solvent in the presence of copper or copper(I) compound and acid-binding agent (139).

CI Vat Brown 3 is prepared from 4,5′-bisbenzoylamino-1,1′-dianthrimide by ring closure in concentrated sulfuric acid. 4,5′-Bisbenzoylamino-1,1′-dianthrimide is prepared from 1-amino-5-benzoylaminoanthraquinone [117-06-6] and 1-benzoylamino-4-chloroanthraquinone [81-45-8] at elevated temperature in an organic solvent in the presence of copper and an acid-binding agent. 1-Amino-5-benzoylaminoanthraquinone is prepared from 1,5-diaminoanthraquinone with benzoyl chloride.

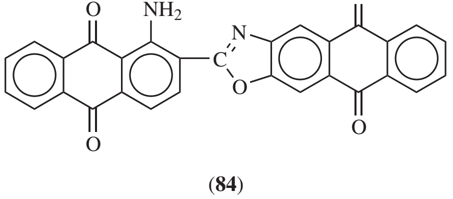
Indanthrene Khaki GG (**80**) is prepared from the corresponding pentanthrimide with aluminum chloride or aluminum chloride–sodium chloride melts.

8.5. Acylaminoanthraquinones. This dye class consists mainly of benzoyl derivatives of aminoanthraquinones. Due to the relatively low molecular weight, this dye class is applied in dyeing at low temperature. Yellow, orange, red, and even violet colors are covered by acylaminoanthraquinones.

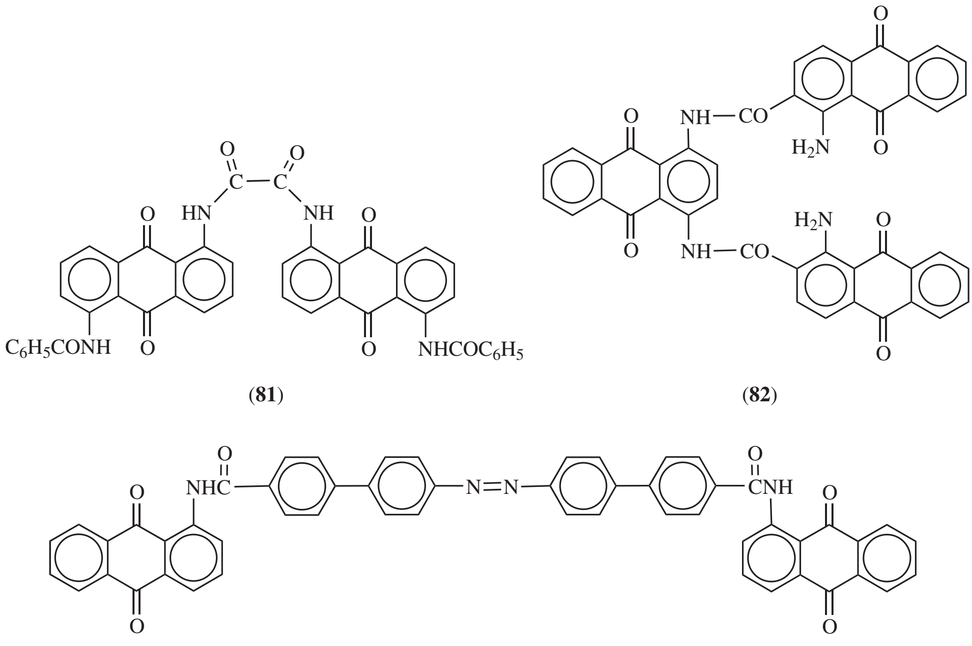
Examples of industrial importance are CI Vat Yellow 12 [6370-75-8] (**81**) (CI 65405), CI Vat Red 21 [4430-70-0] (**82**) (CI 61670), and CI Vat Yellow 33 [12227-50-8] (**83**) (CI 65429) (Fig. 6).

CI Vat Yellow 12 is prepared by condensing 1-amino-5-benzoylaminoanthraquinone [117-06-6] with oxalyl chloride in nitrobenzene. CI Vat Yellow 33 is prepared by condensation of two moles of 1-aminoanthraquinone with one mole of 4′,‴-azobis(4-biphenylcarbonyl chloride). CI Vat Red 21 is prepared from 1,4-diaminoanthraquinone and 1-nitroanthraquinone-2-carboxylic acid.

8.6. Anthraquinoneazoles. The representative anthraquinone oxazole vat dye is CI Vat Red 10 [2379-79-5] (**84**) (CI 67000). This dye is extensively used as a typical red vat dye because of its excellent dyeing properties and fastness. This fastness is considered to be due to hydrogen bonding of the amino hydrogen with an oxygen of the carbonyl group or the oxazole ring.



(**84**)



(**81**) (**82**)

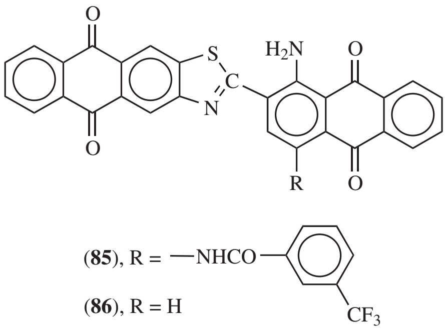
(**83**)

Fig. 6. Acylamino anthraquinone vat dyes.

CI Vat Red 10 is prepared by condensation of 1-nitroanthraquinone-2-carboxylic acid chloride with 2-amino-3-hydroxyanthraquinone followed by ring closure in sulfuric acid and subsequent replacement of the nitro group with aqueous ammonia.

In recent years extensive studies have been carried out to develop a method of synthesis of CI Vat Red 10 starting from 1-aminoanthraquinone-2-carboxylic acid rather than 1-nitroanthraquinone-2-carboxylic acid because of problems with Cr^{6+} in the production of the nitro compound (140,141).

An example of an anthraquinone thiazole that has commercial importance is CI Vat Blue 30 [6492-78-0] (**85**) (CI 67110). This dye exhibits good fastness to light and chlorine.

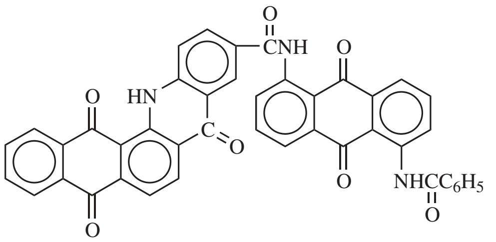


(**85**), R =

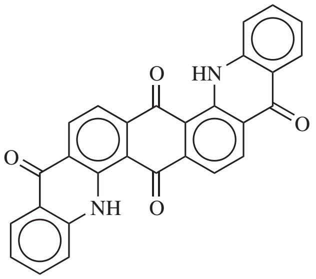
(**86**), R = H

CI Vat Red 20 [6371-49-9] (**86**) (CI 67100) has also been known as an anthraquinone thiazole dye with good fastness. However, this dye is no longer produced commercially because of its duller shade.

8.7. Anthraquinone Acridones. Anthraquinone acridones give a wide range of shades including orange, red, violet, blue, green, and brown with good fastness especially to light. Representatives are CI Vat Orange 13 [6417-38-5] (**87**) (CI 67820), and CI Vat Violet 13 [4424-87-7] (**88**) (CI 68700). CI Vat Orange 13 is prepared from 1-nitroanthraquinone-2-carboxylic acid. CI Vat Violet 13 is prepared from 1,5-dichloroanthraquinone.



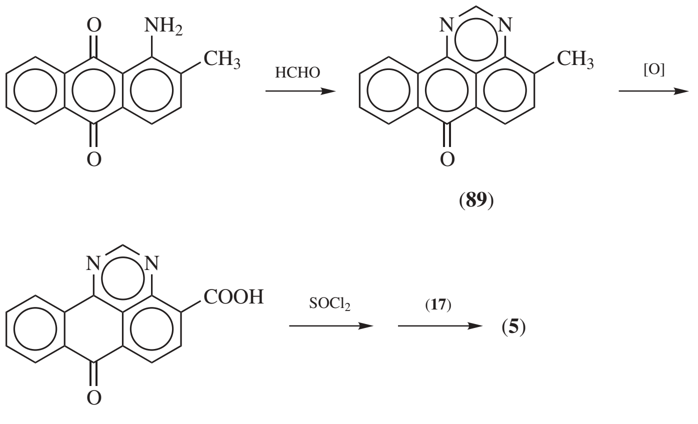
(**87**)



(**88**)

The deeper shades are obtained by addition of other heterocyclic systems, such as quinazoline, to the molecular structure. CI Vat Green 12 [6661-46-7] (CI 70700) is an example.

8.8. Anthrapyrimidines. Anthrapyrimidines are yellow vat dyes and exhibit good fastness. CI Vat Yellow 20 [4216-01-7] (**5**) (CI 68420) is the only example that is currently produced. The production method is shown in the following scheme. This compound is also used as a high performance organic pigment (CI Pigment Yellow 108).

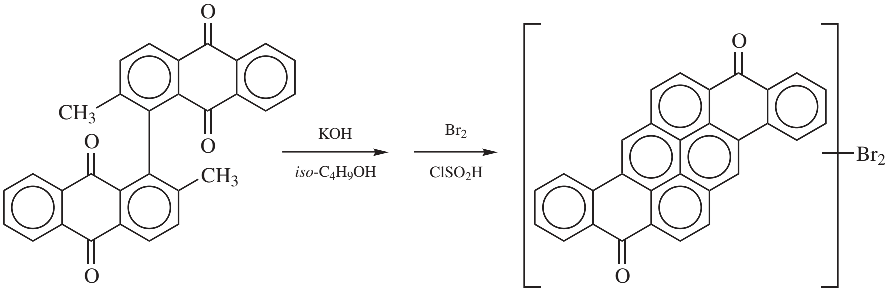


8.9. Other Highly Condensed Ring Systems. *Anthanthrones.* Halogenated derivatives have been developed to improve the dyeing properties of anthanthrones, which have low tinctorial strength and poor affinity to cellulose fibers. The only example of commercial significance is CI Vat Orange 3 [4378-61-4] (**4**) (CI 59300). This compound is prepared from 1,1′-dinaphthyl-8,8′-dicarboxylic acid with oleum and bromine.

Dibenzopyrenquinones. These compounds give brilliant shades from yellow to orange and have high tinctorial power and good dyeing properties. Representatives are CI Vat Yellow 4 [128-66-5] (CI 59100), and its dibrominated derivative CI Vat Orange 1 [1324-11-4] (CI 59105). These dyes are prepared from 1,5-dibenzoylnaphthalene, which can be made by Friedel-Crafts acylation (benzoylation) of naphthalene. An improved method for the oxidative cyclization step using a catalytic amount of ferric halides has been given (142).

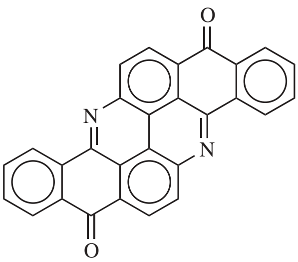
The dibromo derivative exhibits improved fastness to light, washing, and bleach.

Pyranthrones. Pyranthrones give orange shades and halogenated compounds improve lightfastness. A representative that is still widely used industrially is CI Vat Orange 2 [1324-35-3] (**90**) (CI 59705). Its synthesis begins with 1-chloro-2-methylanthraquinone, which is coupled by heating with copper powder in dichlorobenzene–pyridine. Ring closure is effected by KOH in isobutyl alcohol, and the rings are brominated.



(**90**)

Flavanthrone. Flavanthrone [475-71-8] (**91**) (CI 70600) has excellent dyeing properties, which are due to the stability of the leuco form, but its fastness is not satisfactory. Only the unsubstituted flavanthrone is used as a vat dye, ie, CI Vat Yellow 1 (**91**). It is mainly used as a pigment, ie, CI Pigment Yellow 24.



(**91**)

9. Mordant Dyes

Mordant dyes have hydroxy groups in their molecular structure that are capable of forming complexes with metals. Although a variety of metals such as iron, copper, aluminum, and cobalt have been used, chromium is most preferable as a mordant. Alizarin or CI Mordant Red 11 [72-48-0] (**1**) (CI 58000), the principal component of the natural dye obtained from madder root, is the most typical mordant dye. The aluminum mordant of alizarin is a well-known dye by the name of Turkey Red and was used to dye cotton and wool with excellent fastness. However, as is the case with many other mordant dyes, it gave way to the vat or the azoic dyes, which are applied by much simpler dyeing procedures.

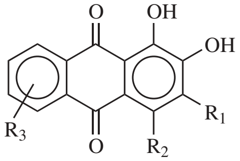
Alizarin is prepared from anthraquinone-2-sulfonic acid by heating with aqueous sodium hydroxide and sodium nitrate at 200°C (143,144).

A variety of derivatives have been produced from alizarin and used as mordant dyes for cotton and wool. Examples are given in Table 6.

Purpurin [81-54-9] (179) is a useful intermediate for preparing acid-mordant dyes, and is prepared by oxidation of alizarin with manganese dioxide and sulfuric acid (145).

Acid–mordant dyes have characteristics similar to those of acid dyes which have a relatively low molecular weight, anionic substituents, and an affinity to polyamide fibers and mordant dyes. In general, brilliant shades cannot be obtained by acid–mordant dyes because they are used as their chromium mordant by treatment with dichromate in the course of the dyeing procedure. However, because of their excellent fastness for light and wet treatment, they are predominantly used to dye wool in heavy shades (navy blue, brown, and black) (146,147).

Table 6. **Alizarin Derivatives as Mordant Dyes**



CI Mordant name or number	R_1	R_2	R_3	Color/Mordant	CAS Registry number	Common name
Red 11	H	H	H	rose red/Al	[72-48-0]	alizarin
Brown 42	OH	H	H	brown/Cr	[602-64-2]	anthragallol
58205	H	OH	H	scarlet/Al	[81-54-9]	purpurin
58215	NO_2	OH	H	red/Al	[6486-91-5]	3-nitropurpurin
Red 45	H	H	5–OH	bordeaux/Al	[6486-93-7]	5-hydroxyalizarin
Red 4	H	H	6–OH	dull red/Cr	[82-29-1]	flavopurpurin

10. Functional Dyes

The investigation of new dyes has always been focused on the development of fast, brilliant, inexpensive, and easy applicable dyes. Because a great emphasis has been placed especially on fastness, the dyes with poorer fastness have been ignored in the past. However, in recent years new needs for dyes that change color in response to low energy stimuli including light, electricity, or heat have arisen in the electronics industry. This application includes information recording, information display, and energy conversion. The term functional dye has been applied to dyes that are used in advanced technologies based on optoelectronics since 1981 when the book entitled *The Chemistry of Functional Dyes* was published in Japan (148).

In order to develop the dyes for these fields, characteristics of known dyes have been re-examined, and some anthraquinone dyes have been found usable. One example of use is in thermal-transfer recording where the sublimation properties of disperse dyes are applied. Anthraquinone compounds have also been found to be useful dichroic dyes for guest-host liquid crystal displays when the substituents are properly selected to have high order parameters. These dichroic dyes can be used for polarizer films of LCD systems as well. Anthraquinone derivatives that absorb in the near-infrared region have also been discovered, which may be applicable in semiconductor laser recording.

10.1. Sublimation Thermal-Transfer Printing. Several methods have been proposed to obtain hard copies of full color images from electronic systems. Among them, sublimation thermal-transfer printing has the following characteristics: the quality of the printed color picture is extremely high, and the equipment is compact, quiet, and easy to manipulate as well as to maintain.

This system consists of a thermal-transfer sheet (ink sheet) containing sublimation dyes, an acceptor sheet containing resin that accepts the sublimated dyes, and a thermal head. The dye in the ink sheet sublimes and is transfer-printed on an acceptor sheet with the thermal energy given by the thermal head. Since the amount of dye transferred can be controlled according to the thermal energy given, good, continuous-gradation color images can be obtained, and full color images can be formed by using ink sheet containing dyes of three primary colors, ie, yellow, magenta, and cyan (see COLOR PHOTOGRAPHY).

The dyes used in the ink sheet must satisfy various requirements: (*1*) optimum color characteristics of the three primary colors (hue, color density, shape of absorption spectrum); (*2*) sensitivity, ie, sublimability from ink sheet to acceptor sheet; (*3*) fastness for light and migration; and (*4*) compatibility with the resin in the ink sheet. With respect to these characteristics, a large number of anthraquinone dyes have been proposed particularly for magenta and cyan colors (149–160).

10.2. Dyes for Liquid Crystal Display Systems. Liquid crystal display systems have been increasingly used in electro-optical devices such as digital watches, calculators, televisions, instrument panels, and displays of various kinds of electronic equipment, ie, lap-top computers and word processors. The dominant reason for their success is their extremely low power consumption. Furthermore, the liquid crystal display systems have been remarkably improved in recent years, and today they have high resolution (more than

300,000 pixels) and full color capability almost equivalent to those of a cathode ray tube.

Guest-Host Mode LCD Systems. Guest-host liquid crystal display systems consisting of dichroic dyes (guest) and liquid crystal media (host) have a wider angle of vision and better color reproducibility than systems that consist of colored polarizers and twisted nematic liquid crystal cells. These dyes are required to satisfy the following criteria: (*1*) brilliant colors with panchromaticity and high extinction coefficient; (*2*) solubility in liquid crystal medium; (*3*) high order parameters; (*4*) stability to light, heat, humidity, and electronic current; (*5*) high purity; and (*6*) high resistivity.

Several basic chromophore structures have been proposed for this purpose. Anthraquinone dyes appear to be predominant since they have a wider color range, excellent photostability, good solubility in liquid crystal media, and very high order parameters. Typical basic structures of the three primary colors are illustrated in Figure 7. The appropriate combination of three primary colors gives a black display (161–165).

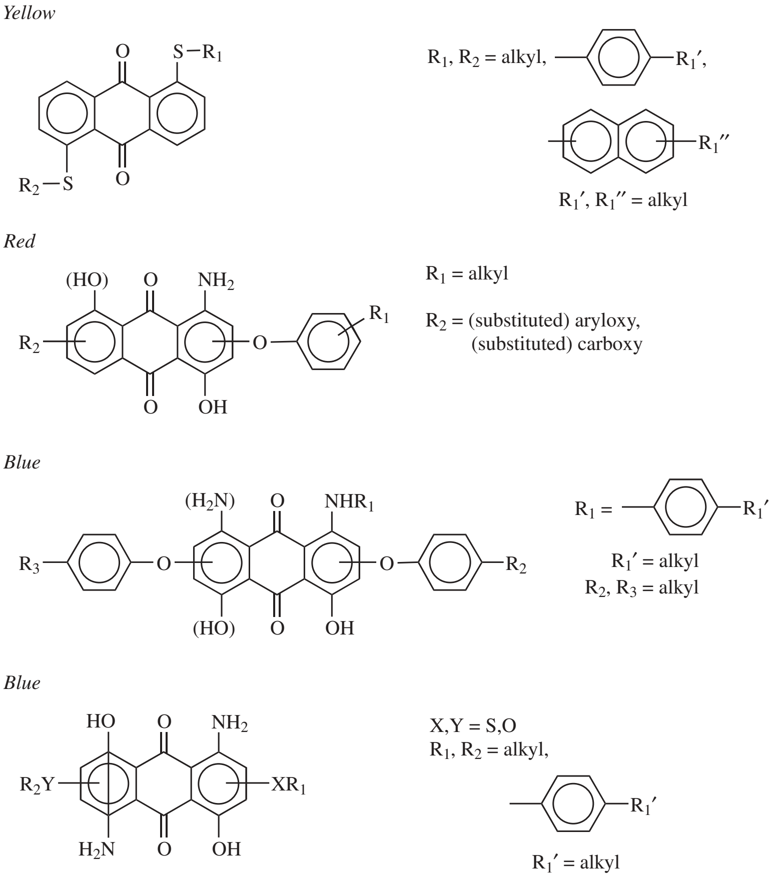


Fig. 7. Basic structural concepts for the three primary color anthraquinone liquid crystal dyes.

Dichroic Dyes for Polarizer Filters. Super twisted nematic liquid crystal display (STN–LCD), now predominant in the market of black and white liquid crystal display systems, consists of a STN cell placed between two polarizers. Most polarizers are poly(vinyl alcohol) films containing iodine molecules aligned in one direction. They have enough quality for the displays of wrist watches, calculators, and other electronic appliances used mainly indoors. However, they have problems due to sublimable iodine, and lack of durability to high temperature, high humidity, and light; they cannot be applied to displays used outdoors or in severe conditions. Polarizers containing dichroic dyes have been intensively studied for such needs as displays of electronic dashboard components for automobiles. Poly(vinyl alcohol) films with dichroic direct dyes and polyester (PET) or polyamide (nylon-6) films containing dichroic disperse dyes have been developed for this purpose. Some anthraquinone disperse dyes have been proposed in the latter system. Dyes having excellent durability and moisture resistance with high polarizing degree have been found (166–169).

Dyes for Color Filters. Color liquid crystal display systems consist of LSI drivers, glass plates, polarizers, electrodes (indium–tin oxide), and microcolor filters. The independent microcolor filter containing dyes is placed on each liquid crystal pixel addressed electrically and acts as an individual light switch. All colors can be expressed by the light transmitted through each filter layer of the three primary colors, ie, red, green, and blue (Fig. 8).

Four significant fabrication processes have been proposed and commercialized so far: a dyeing method using mainly acid or reactive dyes in a gelatin or casein base; a printing method using ink containing pigments and organic vehicles and resins; a pigment dispersion method using photosensitive resins in which pigments are dispersed; and an electrodeposition method using polymer

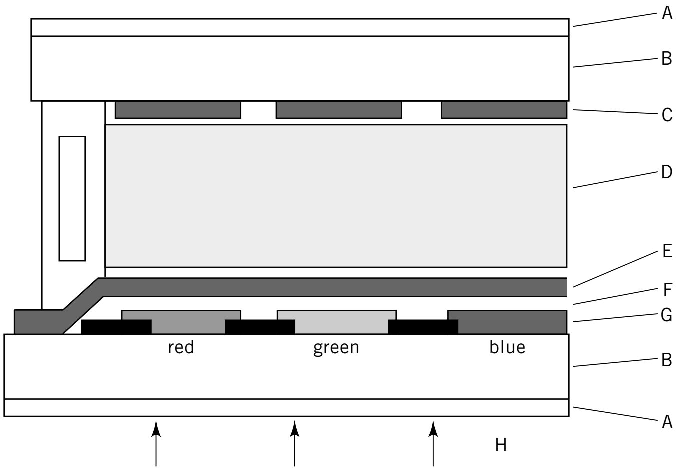
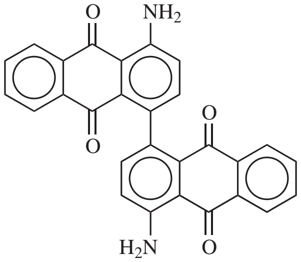


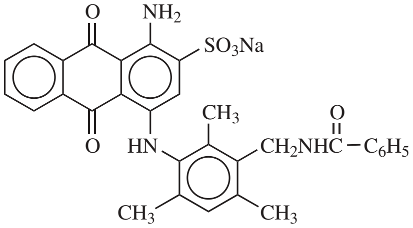
Fig. 8. General structure of LCD. A, polarizer plate; B, glass plate; C, electrodes (indium–tin oxide); D, liquid crystal; E, common electrode (ITO); F, overcoated layer; G, colored pixel; H, back light. In an improved color LCD system today, retardation films are placed between A and B.

resins with pigments dispersed in an aqueous medium and resins electrochemically deposited on electrode (ITO).

The principle of each process is briefly described in the literature (170). Some anthraquinone dyes and pigments appear to be used in combination with other dye or pigment classes such as phthalocyanines and carbazole violets, etc. Two examples described in patents are the red pigment (**92**) and blue dye (**93**) that follow:



(**92**)



(**93**)

The red pigment has been proposed to be usable in both the pigment dispersion method and the electrodeposition method (171,172). The blue dye may be used in the dyeing method fabrication process (173).

10.3. Near-Infrared Absorbing Dyes. Optical disk data storage systems have been increasingly used in offices for document storage (see INFORMATION STORAGE MATERIALS). The disk consists of a polycarbonate base overlaid with a polymer layer containing photosensitive material. Localized thermal changes in this layer can be induced by a semiconductor diode laser, which can be read afterward by optical means. In this system laser light energy is absorbed by the dyes contained in the polymer layer to melt locally and form micropits there. Semiconductor diode lasers emit in the wavelength range around 800 nm, and generally the wavelength range of the AlGaAs laser (780–830 nm) is used. Accordingly, the dyes are required to absorb near-infrared light at this wavelength with a large extinction coefficient. It is also required that the dye has stability to light, resistance to heat and humidity, and solubility in organic solvents. The last is related to coating characteristics. Some anthraquinone dyes have been proposed for this purpose together with other dye or pigment classes such as polymethine dyes, phthalocyanines, and metal complex dyes (174–176).

11. Health and Safety Factors

In general, anthraquinone dyes and their intermediates have not been reported as strongly toxic substances, but for many compounds safety data have not been evaluated. Acute toxicity data (LD_{50}) of some anthraquinone compounds are given in Table 7 (177). 1-Nitroanthraquinone, 1-chloroanthraquinone, and benzanthrone are reported to cause mild skin irritation in a test with rabbits, 500 mg/24 h (177). Some eye irritation data have been reported (177). Most of the compounds cause mild irritation of eyes in a test with rabbits, 500 mg/24 h. These include:

1,2-dihydroxyanthraquinone
1-amino-2,4-dibromoanthraquinone
1-amino-2-bromo-4-hydroxyanthra-quinone
1,4-dihydroxyanthraquinone
1,4-diaminoanthraquinone
1-methylamino-4-bromoanthra-quinone
1,5-dichloroanthraquinone
1,5-dihydroxyanthraquinone
1,5-dimethoxyanthraquinone
1,5-dinitroanthraquinone
1,5-diaminoanthraquinone
1,5-diphenoxyanthraquinone
3-bromobenzanthrone
3,9-dibromobenzanthrone
1-amino-4-hydroxy-2-phenoxy-anthraquinone
1-benzoylamino-5-chloroanthra-quinone
1-amino-5-chloroanthraquinone
1,1′:4,1″-trianthrimide
CI Disperse Blue 56
CI Vat Brown 1
CI Vat Green 1
CI Vat Green 2

Table 7. **Acute Toxicity Data for Some Anthraquinone Compounds**[a]

Compound	Structure number	LD$_{50}$[b] mg/kg
1-nitroanthraquinone	(**18**)	1,540[c]
		1,050
1,5-dinitroanthraquinone	(**37a**)	4,750[c]
		3,130
1-nitroanthraquinone-2-carboxylic acid		2,000[d]
leuco-1,4-diaminoanthraquinone	(**27**)	454[d]
1,4-diaminoanthraquinone	(**28**)	5,790[d]
		250
1,5-dimethoxyanthraquinone		16,600[d]
CI Acid Blue 62	(**67**)	983[e]
benzanthrone	(**44**)	290[e]
		1,500
3-bromobenzanthrone		300[e]
		2,400
4,4′-dibenzanthronyl	(**45**)	1,100[e]
		2,400
3,9-dibromobenzanthrone		1,410[e]
		4,900
CI Vat Blue 20	[f]	2,600[e]
		5,000
1-nitro-2-methylanthraquinone		1,100
1,5-diaminoanthraquinone		1,300
1-aminoanthraquinone	(**17**)	> 10,000[c]
		6,026[e]
		1,500
2-aminoanthraquinone		1,500
1-benzoylamino-4-chloroanthraquinone		2,000
1,4-dihydroxyanthraquinone	(**26**)	2,100
2-amino-3-chloroanthraquinone		2,400
CI Vat Green 1	[f]	2,600
1-amino-4-hydroxyanthraquinone		2,700
1-benzoylamino-5-chloroanthraquinone		3,000
2-chloroanthraquinone		4,310

[a] Ref. 177.
[b] Intraperitonial, rat, unless otherwise noted.
[c] Oral, mouse.
[d] Oral, rat.
[e] Intraperitonial, mouse.
[f] See Table 4 for structure.

A few have been found to be moderate eye irritants in rabbits at 100 mg/24 h, including 1-aminoanthraquinone, 1-nitroanthraquinone, leuco-1,4-diaminoanthraquinone, 1-chloroanthraquinone, and benzanthrone. 4,4′-Dibenzanthronyl is reported to cause severe eye irritation (rabbit, 500 mg/24 h).

There are some tumorigenic data for anthraquinone dyes and intermediates which have been evaluated thoroughly. Data for 2-aminoanthraquinone and 2-methyl-1-nitroanthraquinone are available (88,93). 2-Aminoanthraquinone has been assessed by the United Nations International Agency for Research on Cancer (IARC) from studies in animals, and is judged to fall into the *Animal: Limited Evidence* group. 2-Aminoanthraquinone has been evaluated by EPA (Genetic Toxicology program) and a positive carcinogenic effect for rat and mouse is designated. 2-Methyl-1-nitroanthraquinone has been assessed by IARC and judged as belonging in the *Animal: Sufficient Evidence* group. 2-Methyl-1-nitroanthraquinone has been evaluated by the National Cancer Institute (NCI) and clear evidence of carcinogenicity for rat and mouse is demonstrated.

Most anthraquinone dyes and their intermediates are handled in a powder form. Their dust poses the threat of contact to eyes and skin or contamination of surroundings. Attention must be paid to avoid these hazards. Special attention should be paid to avoid contact with compounds that are recognized to have probable carcinogenicity.

In the case of handling in relatively small quantities, ie, for laboratory use, normal personal equipment, ie, dust masks, safety glasses, and gloves, and hoods with local exhaust ventilation should be used. In plant operations, special technical handling measures should be taken because the possibility of contact is extremely high, especially when charging the raw materials or isolating or packaging the intermediates or final products (see INDUSTRIAL HYGIENE AND PLANT SAFETY).

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MAKOTO HATTORI
Sumitomo Chemical Company
Revised by Staff