Kirk-Othmer Encyclopedia of Chemical Technology.
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TRIPHENYLMETHANE AND RELATED DYES

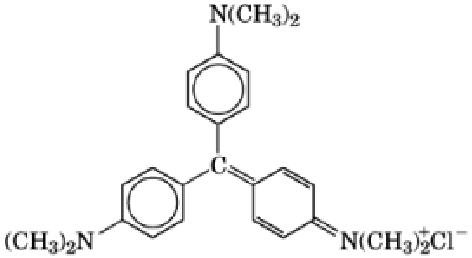
Triphenylmethane dyes comprise one of the oldest classes of synthetic dyes. They are of brilliant hue, exhibit high tinctorial strength, are relatively inexpensive, and may be applied to a wide range of substrates. However, they are seriously deficient in fastness properties, especially fastness to light and washing. Consequently, the use of triphenylmethane dyes on textiles such as wool, silk, and cotton has decreased as dyes from other classes with superior lightfastness and washfastness properties have become available (Dyes and dye intermediates). Interest in this class of dyes was revived with the introduction of polyacrylonitrile fibers (see Acrylonitrile polymers; Fibers, acrylic). Triphenylmethane dyes are readily adsorbed on this fiber and show surprisingly high lightfastness and washfastness properties, compared with the same dyes on natural fibers. However, the durability of acrylic fibers created an even greater demand for fastness properties. Modifications of the classical triphenylmethane dyes intended to improve these properties met with limited success because they were generally accompanied by a reduction in tinctorial strength. Substitution of one of the aryl groups with a heteroaryl residue or the introduction of two or four cyanoethyl groups on the amine functionalities generally increases the lightfastness (1). Research has also led to the development of novel dye types from other chemical classes, such as the pendent cationic dyes, in which the localized positive charge is isolated from the chromophoric system, dyes which were specially designed to give high lightfastness. Similarly, the diazahemicyanine dyes (2), which offer both brightness and fastness, gradually replaced triphenylmethane dyes for incorporation onto acrylic fibers (see Cyanine dyes; Polymethine dyes). Consequently, triphenylmethane dyes are being used in markets where brightness and cost effectiveness, rather than lightfastness and washfastness, are considered to be more important. An example is the coloration of paper. However, triarylmethane dyes such as malachite green [569-64-2] and fuchsine [632-99-5], owing to their high tinctorial strength and low cost, are still used on acrylic fibers as mixtures to produce deep colors, eg, black and navy blue.

The triarylmethane dyes are broadly classified into the triphenylmethanes (CI 42000–43875), diphenylnaphthylmethanes (CI 44000–44100), and miscellaneous triphenylmethane derivatives (CI 44500–44535). The triphenylmethanes are classified further on the basis of substitution in the aromatic nuclei, as follows: (*1*) diamino derivatives of triphenylmethane, ie, dyes of the malachite green series (CI 42000–42175); (*2*) triamino derivatives of triphenylmethane, ie, dyes of the fuchsine, rosaniline, or magenta series (CI 42500–42800); (*3*) aminohydroxy derivatives of triphenylmethane (CI 43500–43570); and (*4*) hydroxy derivatives of triphenylmethane, ie, dyes of the rosolic acid series (CI 43800–43875). Monoaminotriphenylmethanes are known but they are not included in the classification because they have little value as dyes.

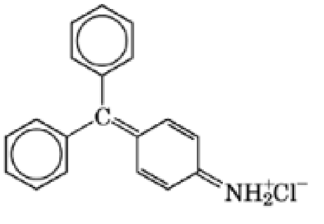
Chemically, the triarylmethane dyes are monomethine dyes with three terminal aryl systems of which one or more are substituted with primary, secondary, or tertiary amino groups or hydroxyl groups in the para position to the methine carbon atom. Additional substituents such as carboxyl, sulfonic acid, halogen, alkyl, and alkoxy groups may be present on the aromatic rings. The number, nature, and position of these substituents determine both the hue or color of the dye and the application class to which the dye belongs. For instance, the triarylmethane dyes that have one amine substituent on only one of the terminal aryl groups give pale yellow dyeings on polyacrylonitrile fibers (3). The introduction of alkyl or alkoxy groups into the other unsubstituted aryl systems can give dyes which produce an orange or red dyeing on polyacrylonitrile fibers (4). Other colors, obtained from the more important commercial triarylmethane dyes, include vivid reds, violets, blues, greens, and even blacks when used in combination with a red azo dye, eg, CI Basic Red 18 [14097-03-1] (CI 11085). The application classes include pigments (qv) and basic (cationic), acidic (anionic), solvent, and mordant dyes. If no acidic groups are present, the dye is cationic or basic. If sulfonic acid groups are present, the dye is anionic or acidic. Carboxylic groups adjacent to hydroxyl groups in the dye confer mordant-dyeing properties. The free bases or the fatty acid salts of the triarylmethane dyes are used as solvent dyes. Pigments can be made by combining a cationic triarylmethane dye with an ion of opposite charge derived from the heteropoly acids of phosphorus, silicon, molybdenum, and tungsten. Pigments can also be made from sulfonated triarylmethane dyes (anionic); the cation is usually barium or calcium.

1. Structure

The first triarylmethane dyes were synthesized on a strictly empirical basis in the late 1850s; an example is fuchsine, which was prepared from the reaction of vinyl chloride with aniline. Their structural relationship to triphenylmethane was established by Otto and Emil Fischer (5) with the identification of pararosaniline [569-61-9] as 4,4′,4″-triaminotriphenylmethane and the structural elucidation of fuchsine. Several different structures have been assigned to the triarylmethane dyes (6–8), but none accounts precisely for the observed spectral characteristics. The triarylmethane dyes are therefore generally considered to be resonance hybrids. However, for convenience, usually only one hybrid is indicated, as shown for crystal violet [548-62-9], CI Basic Violet 3 **(1)**, for which $\lambda_{max} = 589\ \text{nm}$.



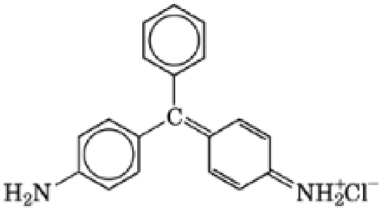
(1)



(2)

The ortho hydrogen atoms surrounding the central carbon atom show considerable steric overlap. Therefore, it can be assumed that the three aryl groups in the dye are not coplanar, but are twisted in such a fashion that the shape of the dye resembles that of a three-bladed propeller (9). Substitution in the para position of the three aryl groups determines the hue of the dye. When only one amino group is present, as in fuchsonimine hydrochloride [84215-84-9], $\lambda_{max} = 440\ \text{nm}$ **(2)**, the shade is a weak orange-yellow.

However, when at least two or more amino groups are present in different rings, the resonance possibility is greatly increased, resulting in a much greater intensity of absorption and in a strong bathochromic shift to longer wavelengths, eg, Doebner's violet [3442-83-9] **(3)**, $\lambda_{\max} = 562$ nm, which is a reddish violet, and pararosaniline **(4)**, $\lambda_{\max} = 538$ nm, which is a bluish violet. The amino derivatives of commercial value contain two or three amino groups.



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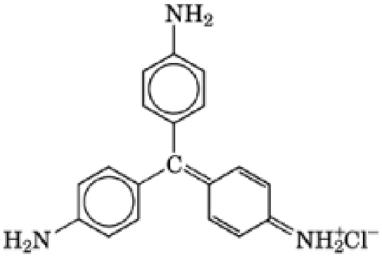
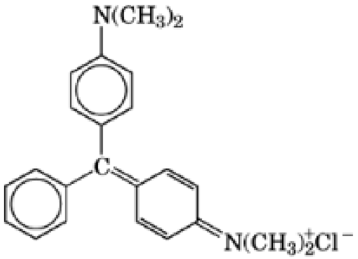


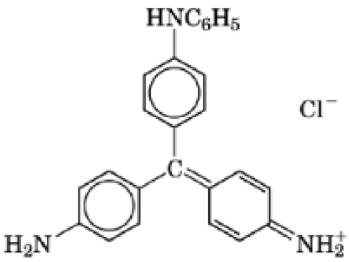
(4)

A further strong bathochromic shift is observed as the basicity of the primary amines is increased by *N*-alkylation, eg, malachite green [569-64-2], CI Basic Green 4, $\lambda_{\max} = 621$ nm **(5)**.



(5)

Phenylation of the primary amino groups also produces an increased bathochromic shift in the wavelength of absorption with increasing degree of phenylation. Only monophenylation of each amino group is possible, eg, as in **(6)** and **(7)**.



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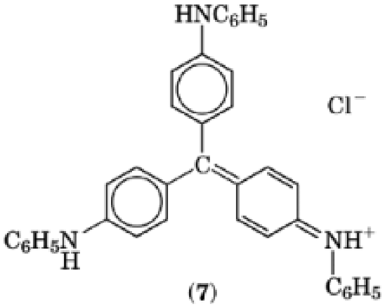
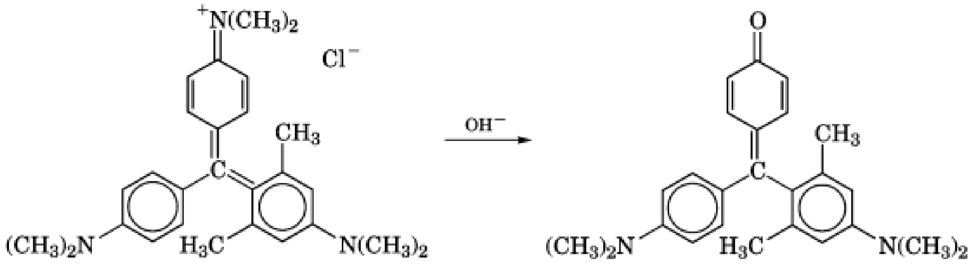


(7)

The steric effects of substituents on the color and constitution of triarylmethane dyes have been studied extensively (10–19). Replacement of the hydrogen atoms ortho to the central carbon atom in crystal violet (λ_{max} = 589 nm) by methyl groups results in a uniform bathochromic shift (ca 8 nm per methyl group) to the 2,2′,2″-trimethyl derivative [84282-50-8] (λ_{max} = 614 nm) and reduced absorptivity values (20). These phenomena suggest that the axial rotational adjustment needed to accommodate the *o*-methyl groups is shared uniformly by the three phenyl rings. The 2,6-dimethyl derivative [117071-61-1] (λ_{max} = 635 nm) **(8)**, however, shows a much larger bathochromic shift per methyl group, and it has been suggested that the dimethylaminoxylyl ring undergoes most of the rotational twist, relieving steric strain by twisting around the central bond in such a way that the charge is localized on the other two dimethylaminophenyl rings. Steric hindrance at the central carbon atom of the 2,6-dimethyl derivative of crystal violet is evident from the fact that the fuchsone derivative [85294-29-7] (λ_{max} = 562 nm) **(9)** and not the corresponding carbinol is formed by the action of a base on the dye **(8)**. Thus, the dimethylamino group on the xylyl ring is partially deconjugated from the central carbon atom, making it less susceptible to nucleophilic displacement; consequently, the base replaces a terminal dimethylamino group on a phenyl ring with hydroxy. Therefore, steric hindrance facilitates the nucleophilic replacement of the terminal dimethylamino group by the hydroxyl group of the base (21).



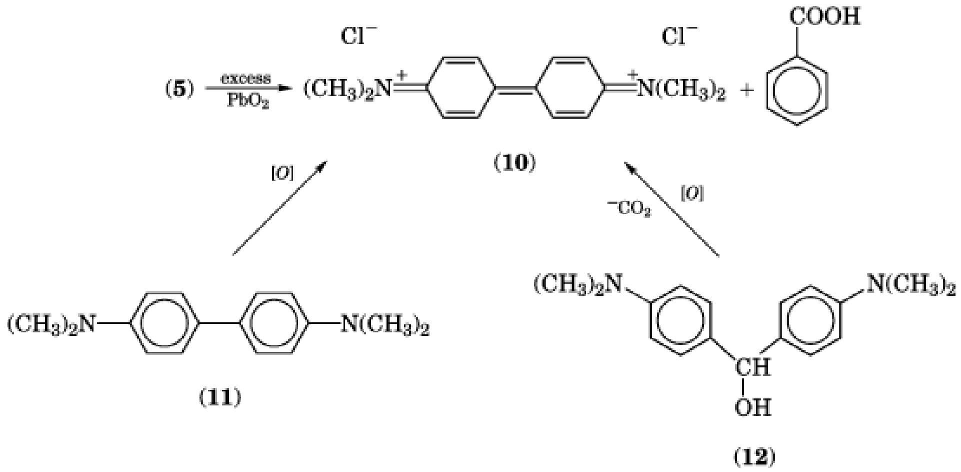
(8) **(9)**

2. Chemical Properties

Dyes in general and triarylmethane dyes in particular are rarely subjected to chemical processing once they have been formed. The introduction of substituents is usually carried out during the manufacture of the intermediates where the position and number of the groups introduced may be more precisely controlled. Dyes are sometimes exposed to oxidizing and reducing conditions during application and afterward.

2.1. Oxidation

Although many triarylmethane dyes are prepared by the oxidation of leuco bases, they are usually destroyed by strong oxidizing agents. Careful choice of both the oxidant and the reaction conditions is required to prevent loss of product during this stage of the manufacture. Overoxidation of malachite green **(5)** gives a quinone imine **(10)** identical to that obtained by oxidizing tetramethylbenzidine **(11)** or Michler's hydrol **(12)**. Overoxidation may also result in the oxidative cleavage of alkyl groups from the amino substituents. Thus, triarylmethane dyes are destroyed by sodium hypochlorite, further limiting their use as textile dyes.



The triarylmethane dyes are extremely sensitive to photochemical oxidation, a fact which accounts for their poor lightfastness on natural fibers (22–31). There are many factors which affect the rate of fading (degradation) of the triarylmethane dyes on natural and synthetic fibers. They include the type of substrate fiber, the nature of the fiber binding site (eg, a sulfonic acid or a carboxylic acid group) to which the dye is attached, the action of oxygen, and, to a lesser degree, water. The photodegradation products of malachite green on cellulosic substrates were identified as benzophenone and 4-dimethylaminobenzophenone (22). It has been proposed that decomposition of triarylmethane dyes occurs upon absorption of ultraviolet radiation by the carbinol form of the dye generated at the dye binding site. The excited carbinol form either undergoes radical fragmentation followed by reaction with water and oxygen or reacts directly with water and oxygen to give the products mentioned above.

Similar degradation products have been identified from the photo-oxidation of crystal violet using singlet oxygen sensitizers (25). In a proposed mechanism, the attack of singlet oxygen on the dye results in the formation of an unstable dioxetane intermediate (a four-membered ring containing two adjacent oxygen atoms). Several studies have revealed that *N*-dealkylation occurs simultaneously with the cleavage and contributes to the photodegradation. Introduction of substituents into the phenyl ring of malachite green produced no marked improvement in the lightfastness because of the presence of the *N*-alkyl groups in the molecule (31).

Replacement with *N*-aryl groups in the analogues of the indolyldiphenylmethane dye, Wool Fast Blue FBL [6661-40-1], however, raised the lightfastness grade by 1–2 points on the 1–8 Gray scale for evaluating color change. Irradiation of *N*-alkyl groups in the presence of air and moisture converts them to aldehydes, eg, formaldehyde or acetaldehyde. Such *N*-dealkylation is a general phenomenon in dye photochemistry, insofar as it has been observed with thiazine dyes (32), rhodamine dyes (33), and *N*-methylaminoanthraquinones (34).

2.2. Reduction

Triarylmethane dyes are reduced readily to leuco bases with a variety of reagents, including sodium hydrosulfite, zinc and acid (hydrochloric, acetic), zinc dust and ammonia, and titanous chloride in concentrated hydrochloric acid. Reduction with titanium trichloride (Knecht method) is used for rapidly assaying triarylmethane dyes. The $TiCl_3$ titration is carried out to a colorless end point which is usually very sharp (see Titanium compounds, inorganic).

$$Ar_3COH + 2\ TiCl_3 + 2\ HCl \longrightarrow Ar_3CH + 2\ TiCl_4 + H_2O$$

2.3. Sulfonation

The direct sulfonation of alkylaminotriphenylmethane dyes gives mixtures of substituted products. Although dyes containing anilino or benzylamino groups give more selective substitution, a sulfonated intermediate such as 3[(*N*-ethyl-*N*-phenylamino)methyl]benzenesulfonic acid (ethylbenzylanilinesulfonic acid) is the preferred starting material. However, Patent Blue V [3546-49-0], CI Acid Blue 3, was made from 3-hydroxybenzaldehyde and two moles of diethylaniline, followed by sulfonation of the leuco base and oxidation to the dye. FD&C Green 2 [5141-20-8], CI Acid Green 5, is still made by trisulfonation of the leuco base using ethylbenzylaniline and benzaldehyde as starting materials.

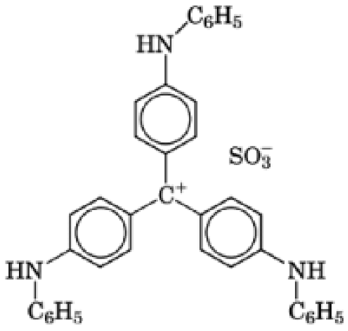
Spirit Blue [2152-64-9], CI Solvent Blue 23 (CI 42760), is one of the few dyes sulfonated as the leuco base. The degree of sulfonation depends on the conditions. Monosulfonated derivatives, commonly referred to as alkali blues, eg, CI Acid Blue 119 [1324-76-1], are used as their barium or calcium salts in printing inks. Disulfonated compounds, eg, CI Acid Blue 48 [1324-77-2], are employed as their sodium or ammonium salts for blueing paper, whereas the trisulfonic derivatives or ink blues, eg, CI Acid Blue 93 [28983-56-4] are used in writing inks (qv).

2.4. *N*-Alkylation and *N*-Arylation

Dyes containing highly alkylated amino groups are prepared from highly alkylated intermediates and not by direct alkylation of dyes carrying primary amino groups. 4,4′,4″-Triaminotriphenylmethane (pararosaniline) may, however, be *N*-phenylated with excess aniline and benzoic acid to give the greenish blue, *N,N′,N″*-triphenylaminotriphenylmethane hydrochloride [2152-64-9], CI Solvent Blue 23 **(7)**, $\lambda_{max} = 586$ nm. Shorter reaction times and use of less benzoic acid give more of a mixture of the reddish blue, mono- and diarylated products.

2.5. Pigment Formation

Triarylmethane dyes can be converted into two types of insoluble compounds (35), which are used industrially as pigments (qv). Both are salts of triarylmethane dyes. Water-soluble cationic dyes are combined with phosphomolybdic acid, phosphotungstomolybdic acid, copper ferricyanide, and occasionally silicomolybdic acid and phosphotungstic acid to form insoluble complexes. Known as pigment lakes, these complexes provide clean, brilliant red and violet shades. These pigments are used in printing inks, especially packaging and special printing inks, but their use, ca 1996, is in decline because of higher production costs compared to other organic pigments that duplicate their color shades. The second type of pigments derived from triarylmethane dyes are known as alkali blues. These are inner salts of sulfonic acids, and the commercially important pigments are derived from either diarylated or triarylated rosaniline, eg, Pigment Blue 61 [1324-76-1] **(13)**, CI 42765.1. They can be prepared by either the diphenylmethane base method or the benzotrichloride method. Concentrated sulfuric acid is required to make the water-insoluble monosulfonates. The main use of the alkali blues is as shading pigments in inks based on carbon black, where an inexpensive blue component is needed to correct the natural brown tone of the base pigment. The main area of application is in printing inks, particularly offset, letterpress, and to a lesser extent in aqueous flexographic inks. They are used to color ribbons for typewriters and also to blue copy paper.



(13)

3. Manufacture

The preparation of triarylmethane dyes proceeds through several stages: formation of the colorless leuco base in acid media, conversion to the colorless carbinol base by using an oxidizing agent, eg, lead dioxide, manganese dioxide, or alkali dichromates, and formation of the dye by treatment with acid (Fig. 1). The oxidation of the leuco base can also be accomplished with atmospheric oxygen in the presence of catalysts.

The major products have been available since the late 1890s, and manufacturing processes have remained unchanged for much of this period. Older syntheses of triarylmethane dyes generally employed the isolation of the leuco base as a filter cake which could be easily washed free of contaminants such as unreacted aromatic amines. The more modern processes, especially the diphenylmethane base and benzotrichloride methods, utilize excess aromatic amines as a convenient solvent to prepare the triarylmethane dyes without the need to isolate any of the intermediates. Consequently, the triarylmethane dyes are isolated as impure materials. The intermediates, by-products, and aromatic amine remain in the dye, reducing the yield and the tinctorial strength of the dye. Purification of the dyes usually involves physical processes, eg, membrane filtration, or chemical processes, eg, salting the mother liquors. These processes reduce the amount of dye isolated, thus adding to the overall cost. Increasingly, there has been a requirement to control effluents and air pollution in most developed countries as environmental controls have become more stringent. The limits for discharging color, acid, alkali, toxic heavy metals (eg, mercury, cadmium, lead, and chromium), lipophilic aromatic amines, or polychlorobiphenyls (PCBs) varies from country to country, but manufacturers have begun to minimize these losses in order to increase the yield of the dye, control the costs, and limit the effluent discharged to the drain. Manufacturing processes to prepare and purify triarylmethane dyes using alternative reagents and technology have appeared regularly in the patent literature since the early 1970s to meet the environmental concerns and lower costs (36–49).

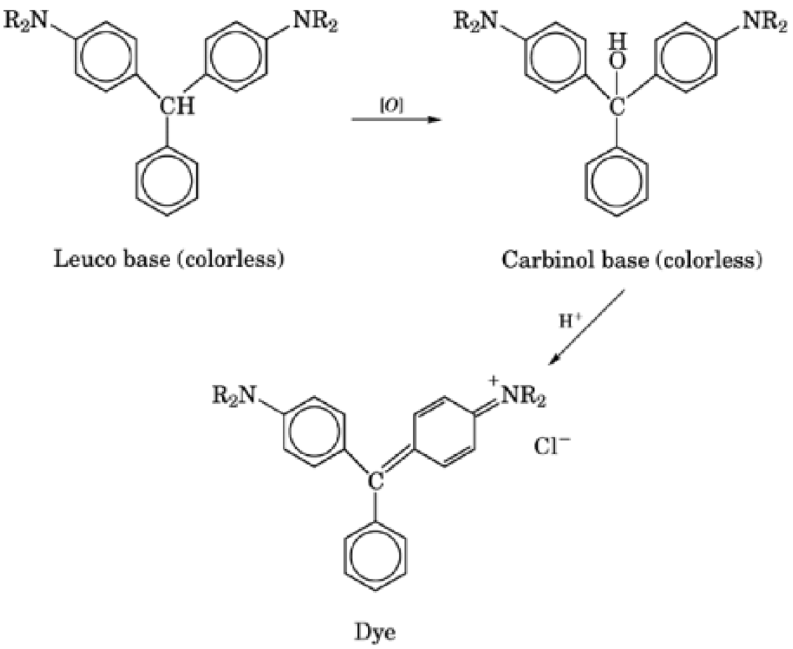


Fig. 1. Preparation of triarylmethane dyes through the colorless leuco base.

3.1. Aldehyde Method

This method is generally used for the preparation of diaminotriphenylmethane dyes or hydroxytriphenylmethane dyes. The central carbon atom is derived from an aromatic aldehyde or a substance capable of generating an aldehyde during the course of the condensation. Malachite green is prepared by heating benzaldehyde under reflux with a slight excess of dimethylaniline in aqueous acid (Fig. 2). The reaction mass is made alkaline and the excess dimethylaniline is removed by steam distillation. The resulting leuco base is oxidized with freshly prepared lead dioxide to the carbinol base, and the lead is removed by precipitation as the sulfate. Subsequent treatment of the carbinol base with acid produces the dye, which can be isolated as the chloride, the oxalate [2437-29-8], or the zinc chloride double salt [79118-82-4].

The leuco base of malachite green has also been oxidized by air using a cobalt complex (36) or an iron complex (37) with chloranil in a mixture of glacial acetic acid and chloroform. Palladium (38), copper (39), vanadium, and molybdenum catalysts (40) have also been used to oxidize the leuco bases to the triphenylmethane dyes. Oxidation of the leuco base to the triarylmethane dye in glacial acetic acid can also be accomplished by treatment with air in the presence of chloranil and gaseous nitrogen oxides (41), eg, nitrogen monoxide and nitrogen dioxide (but not dinitrogen oxide). Under the acidic reaction conditions, other catalysts which release these nitrogen oxides can also be used, eg, iron(III) nitrate and sodium nitrite. Oxidative electrolysis has also been used to convert the leuco base to triarylmethane dyes (48).

The starting materials of the aldehyde method may be sulfonated. For example, CI Acid Blue 9 [2650-18-2], CI Food Blue 2 (CI 42090), is manufactured by condensing *α*-(*N*-ethylanilino)-*m*-toluenesulfonic acid with *o*-sulfobenzaldehyde. The leuco base is oxidized with sodium dichromate to the dye, which is usually isolated as the ammonium salt. In this case, the removal of the excess amine is not necessary. However, this color cannot be used in the food sector because separation of the chromium compounds from the dye is difficult. An alternative method which gives food-grade CI Acid Blue 9 **(14)** and dispenses with the use of sodium dichromate employs oxidative electrolysis of the leuco base (49).

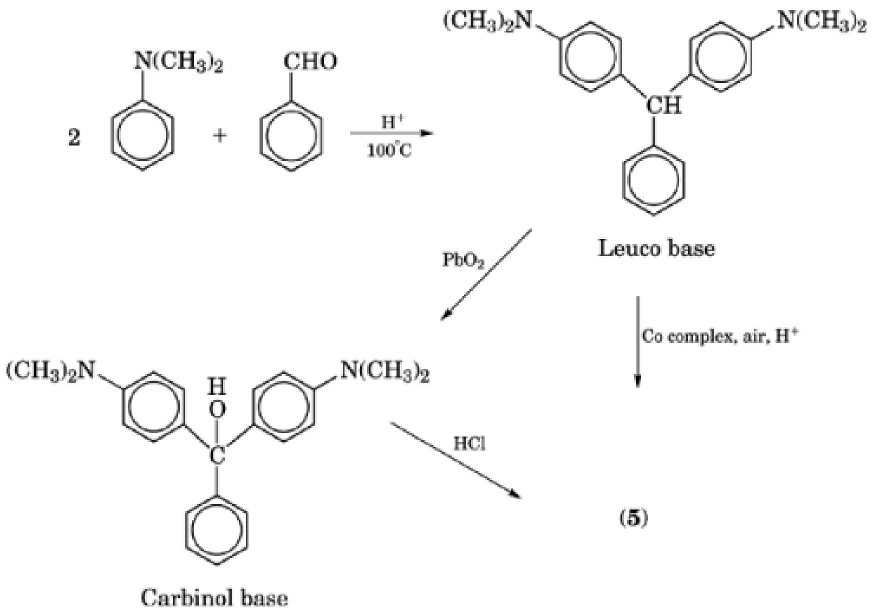
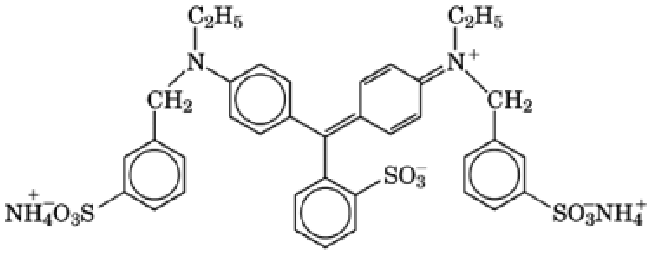


Fig. 2. Preparation of malachite green (**5**).



(14)

4. Ketone Method

In the ketone method, the central carbon atom is derived from phosgene (qv). A diarylketone is prepared from phosgene and a tertiary arylamine and then condenses with another mole of a tertiary arylamine (same or different) in the presence of phosphorus oxychloride or zinc chloride. The dye is produced directly without an oxidation step. Thus, ethyl violet [2390-59-2], CI Basic Violet 4 **(15)**, is prepared from 4,4′-bis(diethylamino)benzophenone with diethylaniline in the presence of phosphorus oxychloride. This reaction is very useful for the preparation of unsymmetrical dyes. Condensation of 4,4′-bis(dimethylamino)benzophenone [90-94-8] (Michler's ketone) with *N*-phenyl-1-naphthylamine gives the Victoria Blue B [2580-56-5], CI Basic Blue 26, which is used for coloring paper and producing ballpoint pen pastes and inks.

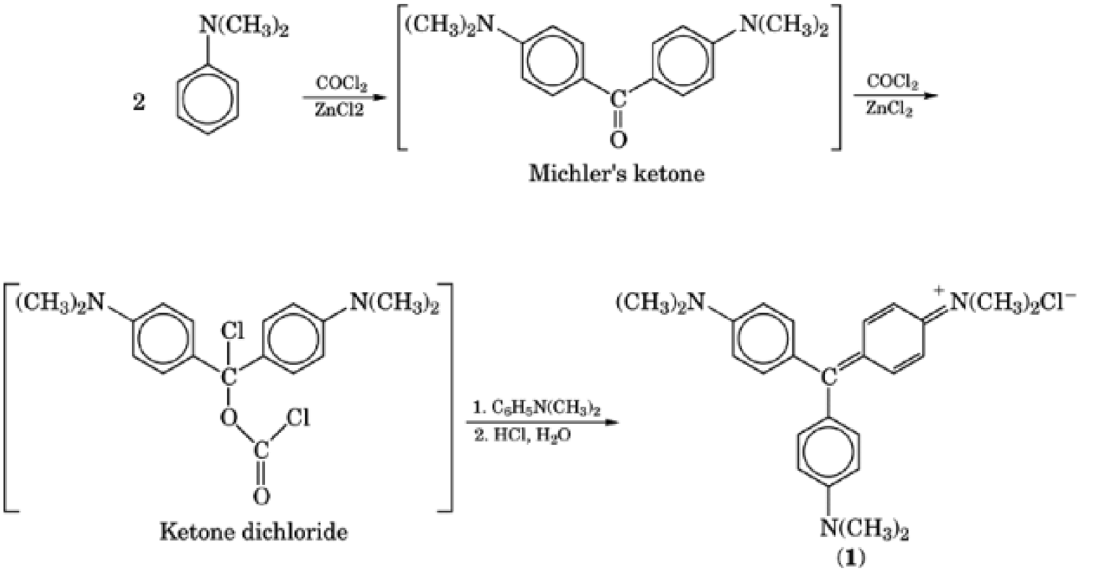
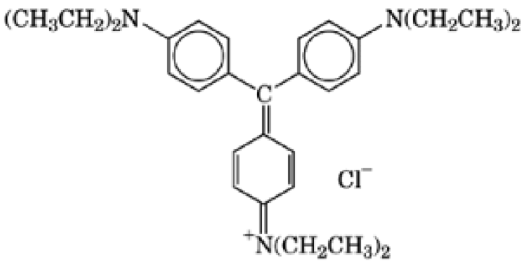


Fig. 3. Manufacture of crystal violet (**7**).



(15)

The manufacture of crystal violet **(1)**, however, is a special case which does not involve the isolation of the intermediate Michler's ketone (Fig. 3). Thus, phosgene is treated with excess dimethylaniline in the presence of zinc chloride. Under these conditions, the highly reactive intermediate "ketone dichloride" is formed in good yield; this intermediate further condenses with another mole of dimethylaniline to give the dye.

4.1. Diphenylmethane Base Method

In this method, the central carbon atom is derived from formaldehyde, which condenses with two moles of an arylamine to give a substituted diphenylmethane derivative. The methane base is oxidized with lead dioxide or manganese dioxide to the benzhydrol derivative. The reactive hydrols condense fairly easily with arylamines, sulfonated arylamines, and sulfonated naphthalenes. The resulting leuco base is oxidized in the presence of acid (Fig. 4).

In a variation of this method, isolation of the benzhydrol derivative is not required. The methane base undergoes oxidative condensation in the presence of acid with the same or a different arylamine directly to the dye. New fuchsine [3248-91-7], CI Basic Violet 2 **(16)**, is prepared by condensation of two moles of *o*-toluidine with formaldehyde in nitrobenzene in the presence of iron salts to give the corresponding substituted

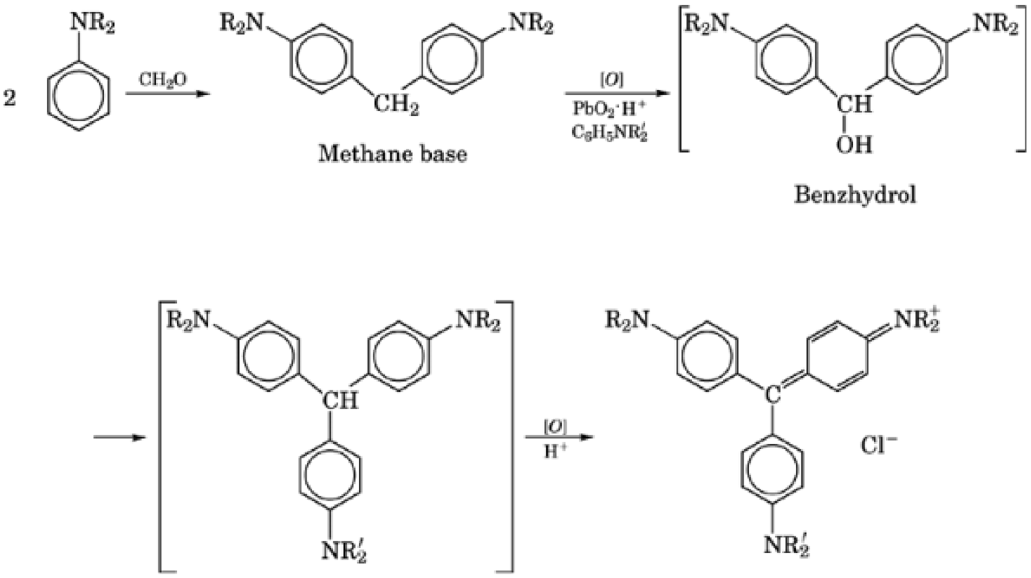
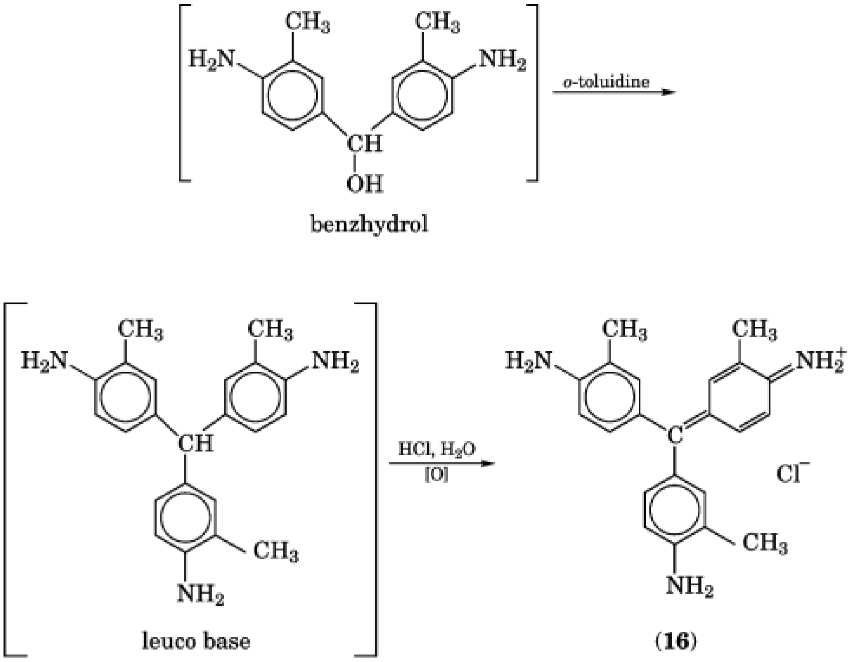


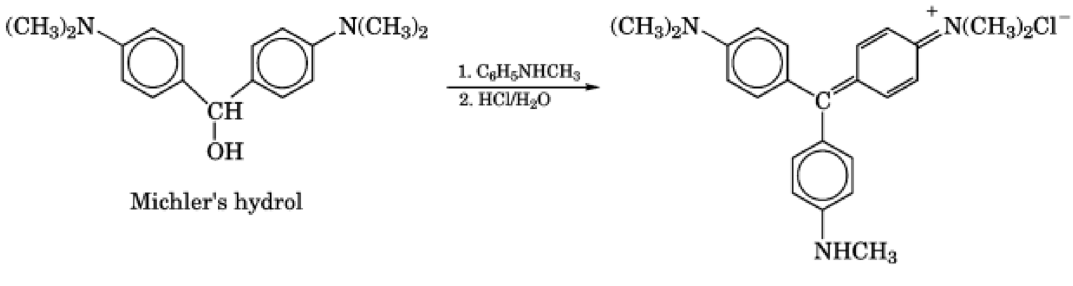
Fig. 4. Diphenylmethane base route to triarylmethane dyes.

diphenylmethane base. This base is also not isolated, but undergoes an oxidative condensation with another mole of *o*-toluidine to produce the dye.



(**16**)

Methyl violet [8004-87-3], CI Basic Violet 1 **(17)**, is made by the air oxidation of dimethylaniline in the presence of salt, phenol, and a copper sulfate catalyst. Initially, some of the dimethylaniline is oxidized to formaldehyde and *N*-methylaniline under those conditions. The formaldehyde then reacts with dimethylaniline to produce *N,N,N′,N′*-tetramethyldiaminodiphenylmethane, which is oxidized to Michler's hydrol [119-58-4]. The hydrol condenses with *N*-methylaniline formed in the initial step to give the leuco base of methyl violet. Treatment with aqueous acid produces the dye. Because Michler's hydrol may also react with dimethylaniline instead of the *N*-methylaniline to give crystal violet, commercial-grade methyl violet is usually a mixture. A cobalt complex has converted 4,4′-dimethylaminodiphenylmethane and dimethylaniline in the presence of atmospheric oxygen to crystal violet in one step (50).



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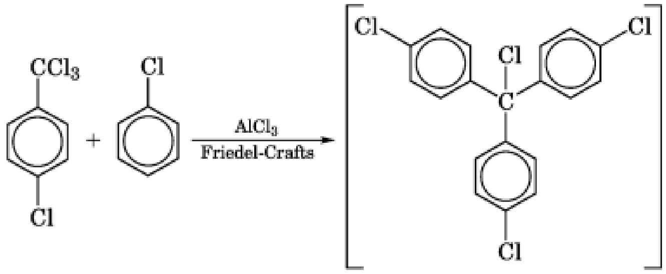
4.2. Benzotrichloride Method

The central carbon atom of the dye is supplied by the trichloromethyl group from *p*-chlorobenzotrichloride. Both symmetrical and unsymmetrical triphenylmethane dyes suitable for acrylic fibers are prepared by this method. 4-Chlorobenzotrichloride is condensed with excess chlorobenzene in the presence of a Lewis acid such as aluminium chloride to produce the intermediate aluminium chloride complex of 4,4′,4″-trichlorotriphenylmethyl chloride **(18)**. Stepwise nucleophilic substitution of the chlorine atoms of this intermediate is achieved by successive reactions with different arylamines to give both symmetrical (51) and unsymmetrical dyes (52), eg, *N*-(2-chlorophenyl)-4-[(4-chlorophenyl)[4-[(3-methylphenyl)imino]-2,5-cyclohexadien-1-ylidene]methyl]benzenamine monohydrochloride [85356-86-1] **(19)** from *m*-toluidine and *o*-chloroaniline.



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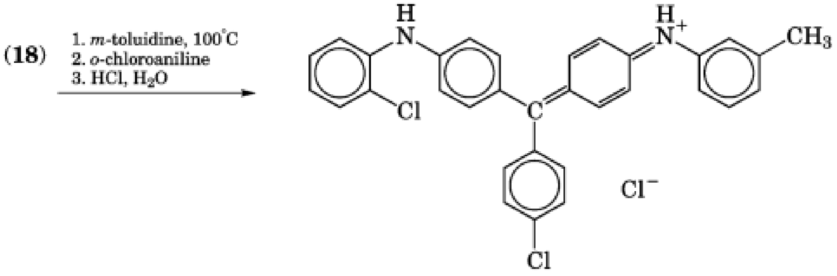


(19)

5. Economic Aspects

Since 1973, the U.S. International Trade Commission has reported the manufacture and sales of dyes by application class only. In 1972, the last year for which statistics are available by chemical class, 3900 metric tons of triarylmethane dyes were manufactured, which represents approximately 4% of total dyestuff production in the United States. At that time, there were 185 triarylmethane dyes listed in the *Colour Index.* From the latter half of the 1970s through the 1980s, annual dye production in the United States, including triarylmethane dyes, changed very little. In 1981, methyl violet, with an annual production of 725 t, was the only triarylmethane dye for which production statistics were available. Some triarylmethane dyes were imported, eg, malachite green (163 t in 1981), methyl violet (40 t), new fuchsine (30 t), and other dyes totalling less than 15 t.

Statistics for the production of basic dyes include those products listed as cationic dyes, eg, cyanines, for dyeing polyacrylonitrile fibers and the classical triarylmethane dyes, eg, malachite green, for coloring paper and other office applications (2, 53). Moreover, statistics for triarylmethane dyes are also hidden in the production figures for acid, solvent, mordant, and food dyes, and also organic pigments. Between 1975 and 1984, the annual production of basic dyes in the United States varied from 5000–7700 t. However, from 1985–1990, annual production of basic dyes varied from 5000–5700 t, and the annual sales value increased from $56 to $73 million per year.

6. Health, Safety, and Environmental Information

In the 1960s, problems were encountered with the interpretation of toxicological studies on animals given triarylmethane dyes used as food colorants (54). The disagreement between experts largely persuaded certain authorities (U.K. and EEC) to remove Brilliant Blue FCF, CI Food Blue 2 (CI 42090), from the permitted lists. Although Brilliant Blue FCF was reinstated on the U.K. list, as of 1997 the problem still exists of correlating laboratory tests and actual human exposure. Conflicting test data have been obtained on various triarylmethane dyes (55). Positive and negative results for the same dye in different assays have only led to more genotoxic studies. For example, both Fast Green FCF [2353-45-9], CI Food Green 3 (CI 42053), and Green S [3087-16-9], CI Food Green 4 (CI 44090), have been subjected to many screenings and are permitted in food in several countries. However, other triarylmethane dyes have been proved genotoxic, eg, Acid Violet 6B [1694-09-3], CI Food Violet 2 (CI 42640), Methyl Violet 2B, CI Basic Violet 1 (CI 42535), and Victoria Blue B, CI Basic Blue 26 (CI 44045). These dyes are approved for limited use in food in some countries, however in the United States, CI Food Violet 2 was delisted for use in food, drugs, and cosmetics in 1973. There are triarylmethane dyes which have also been delisted worldwide for use in food, eg, Guinea Green B [4680-78-8], CI Food Green 1 (CI 42085), and Violet BNP [80539-34-0], CI Food Violet 3.

The triarylmethane dyes of the rosaniline family, eg, fuchsine and crystal violet, show similar toxic responses in assays. They are moderately toxic after acute exposure, but the effects usually pass within a couple of days. These effects are no cause for alarm as long as the dyes are not permitted for food use or contact (56). There is evidence that the toxicological effects might be the result of impurities, eg, aromatic amines, or of certain functional groups, notably amino substituents found in the dyes (55). The metabolic fate of the triarylmethane dyes in humans or animals has also been studied (54, 57). Most dyes show almost quantitative excretion and no detectable coloring in the urine or metabolites in the body fluids. There have been many studies on the incidence of cancers among dye workers and users. Cancers among workers have declined since the use of the dye intermediates benzidine and β-naphthylamine were restricted in many developed countries. By the 1970s, it was thought that there was no evidence that human cancers were caused by dyes or pigments even if they showed animal carcinogenicity (58). There is very little information about the effects of triarylmethane dyes in products used by the consumer.

The toxicity of dyes to aquatic organisms has also been investigated (59), with most of the work done on fish. In these studies, over 3000 dyes in common use were tested, of which 27 dyes had a LC_{50} around 0.05 mg/L. Ten of these cases had triarylmethane structures. The American Dye Manufacturers Institute (AMDI) has also actively investigated this area. In their studies, the dye of highest toxicity was CI Basic Violet 1 with a LC_{50} of 0.05 mg/L (60). Environmental regulations have made it necessary to examine whether the dyes are toxic, biodegradable, accumulate in fish, or persist in such a way that they could prove hazardous for any downstream uses (see Dyes, environmental chemistry). The Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) and AMDI have built up a body of knowledge concerning the toxicity and environmental impact of many dyestuffs, including triarylmethane dyes.

7. Environmental Concerns

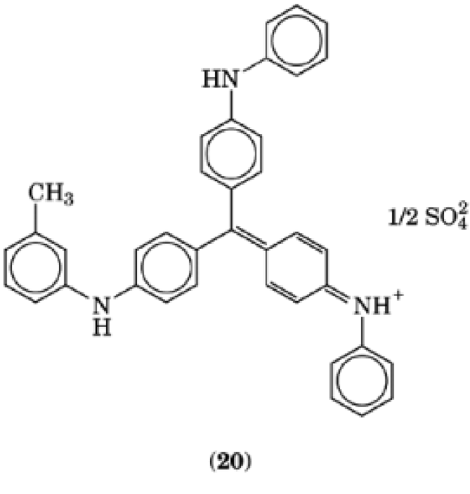
The main route by which dyes enter the environment is via wastewater, both from their manufacture and their use. Accurate data on dyes released into the environment are not available, although lists of materials released to the environment from the processes operated for the production of some triarylmethane dyes have been reported (61). However, various estimates and calculations have suggested that 1–2% of a dye is lost at the manufacturing stage and 1–10% is lost at the user stage (62). One estimate revealed that 2–3% of a basic dye is lost in exhaust and wash liquors. Manufacturers of dyes have increasingly investigated various technologies for effluent treatment, and some discussion of the treatment of triarylmethane dye waste has appeared in the literature (63, 64).

8. Uses

Present usage of triarylmethane dyes, ca 1996, is confined mainly to nontextile applications. Substantial quantities are used in the preparation of organic pigments for printing inks, pastes, and for the paper printing trade, where cost and brilliance of shade are more important than lightfastness. Triarylmethane dyes and their colorless precursors, eg, carbinols and lactones, are used extensively in heat-, light-, and pressure-sensitive recording materials for high speed photoduplicating and photoimaging systems and for the production of printing plates and integrated circuits. They are also used for specialty applications such as tinting automobile antifreeze solutions and toilet sanitary preparations, in the manufacture of carbon paper, in ink for typewriter ribbons, and ink jet printing for high speed computer printers.

In addition to the dyeing and printing of natural and acrylic fibers, triarylmethane dyes are suitable for the coloration of other substrates such as paper, ceramics, leather, fur, anodized aluminium, waxes, polishes, soaps, plastics, drugs, and cosmetics. Several triarylmethane dyes are used as food colorants and are manufactured under stringent processing controls (see Colorants for foods, drugs, cosmetics, and medical devices). They are usually bright green and blue, but red and violet shades are available for food coloring. Triphenylmethane dyes are also used extensively as microbiological stains. Some triarylmethane derivatives are very effective mothproofing agents for wool. Their use as antihalation dyes for photographic materials and as indicators is mentioned in the literature.

Triarylmethane dyes can be used for the coloration of glass. Using water-soluble dyes, eg, CI Acid Blue 83 [6104-59-2] (CI 42660), it is possible to prepare color filters by photomicrolithography. A red, green, and blue matrix of the three primary colors can be built up on the glass to produce the color filters. Several Japanese companies are investigating this technology to produce flat screen televisions. Other high technology applications using triarylmethane dyes include electrophotography and optical data storage. As the number of photocopying machines using selenium has decreased, organic photoconductors, especially positive charge control agents (CCAs), have become more important. Triarylmethane dyes such as *N*-{4-(bis[4-(phenylamino)phenyl]methylene)-2,5-cyclohexadien-1-ylidene}-3-methyl-benzeneamine sulfate [57877-94-8] **(20)** have been claimed as positive CCAs (65). The absorption spectra of the triarylmethane dyes can be extended into the near-infrared region. The use of triarylmethane dyes as infrared absorbers for optical information recording media (66) and as infrared color formers in carbonless copy paper has been claimed.

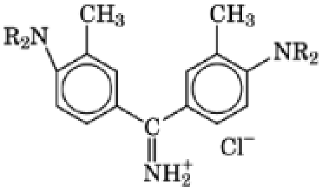


(20)

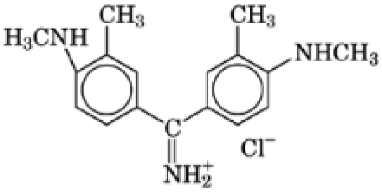
9. Related Dyes

9.1. Diphenylmethane Dyes

The diphenylmethane dyes are usually classed with the triarylmethane dyes. The dyes of this subclass are ketoimine derivatives, and only three such dyes are registered in the *Colour Index.* They are Auramine O [2465-27-2] CI Basic Yellow 2 (CI 41000) (**21**, $R = CH_3$), Auramine G [2151-60-2] CI Basic Yellow 3 (CI 41005) **(22)**, and CI Basic Yellow 37 [6358-36-7] (CI 41001) (**21**, $R = C_2H_5$). These dyes are still used extensively for the coloration of paper and in the preparation of pigment lakes.



(21)

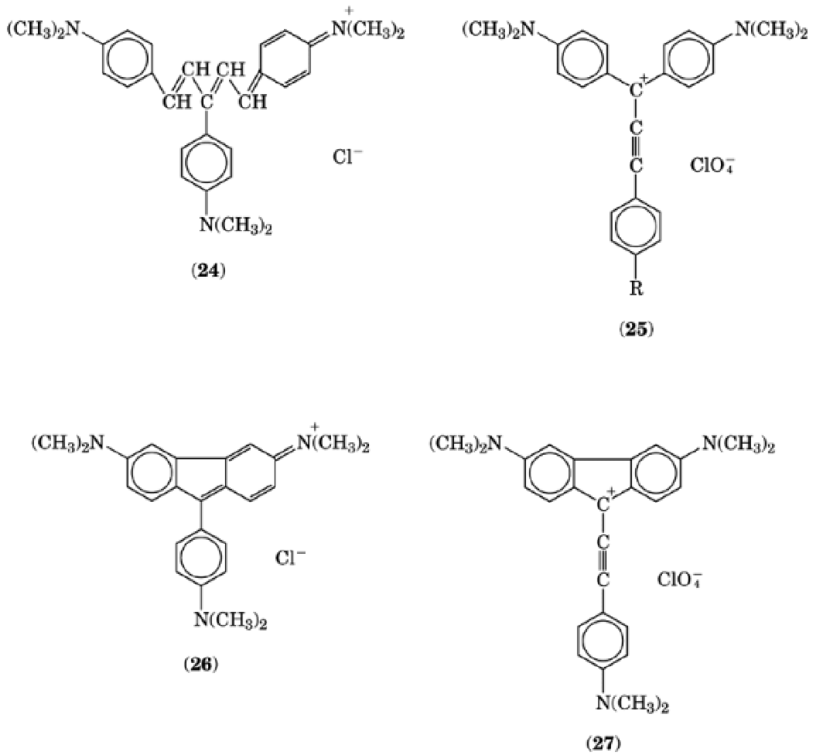


(22)

Auramine O is manufactured by heating 4,4′-bis(dimethylaminodiphenyl)methane with a mixture of urea, sulfamic acid, and sulfur in ammonia at 175°C. The auramine sulfate [52497-46-8] formed in the reaction may be used directly in the dyeing process or can be converted into auramine base [492-80-8]. Highly concentrated solutions for use in the paper industry can be prepared by dissolving auramine base in formamide containing sodium bisulfate. The nitrate and nitrite salts exhibit excellent solubility in alcohols, which facilitates their use in lacquers and flexographic printing colors. Alkyl and halogen derivatives of *N*-phenyl(leucauramine) are colorless, stable, crystalline compounds that turn dark blue when in contact with acidic inorganic compounds such as aluminium sulfate, zinc sulfate, bentonite, or kaolin. They are useful in the production of colorless transfer sheets that on contact with an acidic copying sheet yield blue prints.

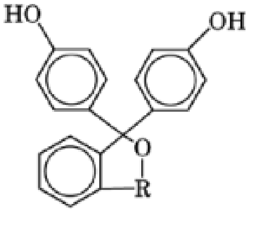
9.2. Phthaleins

Dyes of this class are usually considered to be triarylmethane derivatives. Phenolphthalein [77-09-8] (**23**, $R = CO$) and phenol red [143-74-8] (**23**, $R = SO_2$) are used extensively as indicators in colorimetric and titrimetric determinations (see Hydrogen-ion activity). These compounds are prepared by the condensation of phenol with phthalic anhydride or *o*-sulfobenzoic anhydride, respectively, in the presence of a dehydrating agent.



(**24**) (**25**) (**26**) (**27**)

Fig. 5. Triarylmethane dyes with near-infrared absorption. For (**24**) [76438-66-9] in acetic acid, λ_{max}=770 nm. For (**25**), if R=H [47544-33-2], $\lambda_{max}(CH_2Cl_2)$=688 nm and log$E$=5.00; if R=N$(CH_3)_2$ [118751-95-4], $\lambda_{max}(CH_2Cl_2)$=663 nm and log$E$=5.12. For the 9-arylfluorenone (**26**) [35324-95-9], λ_{max}=647 and 850 nm; for (**27**) [127877-25-2], $\lambda_{max}(CH_2Cl_2)$=956 nm and log$E$=4.18.



(**23**)

9.3. Heteroarylmethane Dyes

Dyes of this class usually have either one or two heteroaryl groups attached to the methane carbon atom. Trihetarylmethane dyes are known and have been investigated for their pharmacological activity (67–69) as well as their color characteristics. Dyes with only one heteroaryl substituent are prepared by the condensation of a diarylketone with the heteroaryl, eg, indole or carbazole. These dyes produce blue, green, and black dyeings on polyacrylonitrile fibers, whereas the dyes with two heteroaryl substituents produce red, violet, and blue dyeings. Dyes with two heteroaryl groups are prepared similarly, by condensation of an arylhetarylketone with a heteroaryl. These types of triarylmethane dyes and their derivatives are used as color formers in thermoreactive and pressure-sensitive recording materials (70–73).

9.4. Triarylmethane Dyes with Near-Infrared Absorption

The long wavelength absorption bands of triarylmethane dyes can be shifted into the near-infrared region, but the dyes still remain colored because other absorption bands are shifted to or stay in the visible region. There are two methods for shifting the absorption into the near-infrared region (74–76). The first method is to extend the chromophore by inserting extra conjugation, eg, carbon–carbon double (**24**) or triple bonds (**25**), or *p*-phenylene groups, between the methane carbon atom and the aryl groups. The second method involves linking two of the aryl rings at their 2- and 2′-positions with a direct bond to give a 9-arylfluorene derivative (5, 5). These types of triarylmethane dyes and their derivatives have been claimed as infrared absorbers for optical information recording media (66) and security devices (77), and as organic photoconductors for use in lithographic plate production (78) (Fig. 5).

BIBLIOGRAPHY

"Triphenylmethane and Diphenylnaphthylmethane Dyes" in *ECT* 1st ed., Vol. 14, pp. 302–329, by A. J. Cofrancesco, General Aniline & Film Corp.; "Triphenylmethane and Related Dyes" in *ECT* 2nd ed., Vol. 20, pp. 672–737, by V. G. Witterholt, E. I. du Pont de Nemours & Co., Inc.; in *ECT* 3rd ed., Vol. 23, pp. 399–412, by D. Bannister and J. Elliott, Ciba-Geigy Corp.

Cited Publications

1. Brit. Pat. 1,195,004 (Jan. 12, 1968), H. P. Kuelthau and R. Raue (to Bayer); Brit. Pat. 1,191,190 (Mar. 10, 1967), U. Blass (to Sandoz).
2. R. Raue, *Rev. Prog. Coloration*, **14**, 187–203 (1984).
3. Fr. Pat. 1,098,497 (Apr. 24, 1953) (to Ciba).
4. Ger. Pat. 1,811,652 (Nov. 29, 1968), R. Raue, H. P. Kuehlthau, and W. Eifler (to Bayer); see also U.S. Pat. 3,647,349 and U.S. Pat. 4,115,413.
5. O. Fischer and E. Fischer, *Ber.* **11**, 1079 (1878).
6. R. Wizinger, *Ber.* **60**, 1377 (1927).
7. C. R. Bury, *J. Am. Chem. Soc.* **57**, 2115 (1935).
8. L. Pauling, *Proc. Nat. Acad. Sci. USA*, **25**, 577 (1939).
9. W. Klyne and P. B. D. de la Mare, *Progress in Stereochemistry*, Vol. **2**, Academic Press, Inc., New York, 1958, p. 42.
10. C. C. Barker, in G. W. Gray, ed., *Steric Effects in Conjugated Systems*, Butterworths, London, 1958, p. 34.
11. C. C. Barker, G. Hallas, and A. Stamp, *J. Chem. Soc.* **82**, 3790 (1960); C. C. Barker and G. Hallas, *J. Chem. Soc.* **83**, 1529 (1961).
12. G. Hallas, *J. Soc. Dyers Colour.* **83**, 368 (1968).
13. D. E. Grocock, G. Hallas, and J. D. Hepworth, *J. Soc. Dyers Colour.* **86**, 200 (1970); A. S. Ferguson and G. Hallas, *J. Soc. Dyers Colour.* **87**, 187 (1971).
14. A. S. Ferguson and G. Hallas, *J. Soc. Dyers Colour.* **89**, 22 (1973).
15. G. Hallas, K. N. Paskins, D. R. Waring, J. R. Humpston, and A. M. Jones, *J. Chem. Soc., Perkin Trans. II*, 450 (1977).
16. B. M. Fox, J. D. Hepworth, D. Mason, J. Sawyer, and G. Hallas, *J. Soc. Dyers Colour.* **98**, 10 (1982).
17. G. Hallas and M. M. Mitchell, *J. Soc. Dyers Colour.* **102**, 15 (1986).
18. S. F. Beach and co-workers, *J. Chem. Soc. Perkin Trans. II*, 1087 (1989).
19. H. Nakazumi, T. Kuriyama, and T. Kitao, *Shikizai Kyokaishi*, **59**, 747 (1986); H. Nakazumi, T. Kuriyama, Y. Shiraishi, and T. Kitao, *Shikizai Kyokaishi*, **60**, 420 (1987).
20. S. S. Ghandi, G. Hallas, and J. Thomasson, *J. Soc. Dyers Colour.* **93**, 451 (1977).
21. C. C. Barker and G. Hallas, *J. Chem. Soc.* **83**, 2642 (1961).
22. J. J. Porter and S. B. Spears, *Text. Chem. Color.* **2**, 191 (1970).
23. N. S. Allen, J. F. McKellar, and B. Mohajerani, *Dyes Pigm.* **1**, 49 (1980); N. S. Allen, *Rev. Prog. Color.* **17**, 61 (1987).

24. I. H. Leaver, *Photochem. Photobiol.* **16**, 189 (1972).
25. N. Kuramato and T. Kitao, *Dyes Pigm.* **3**, 49 (1982).
26. K. Iwamoto, *Bull. Chem. Soc. Jpn.* **10**, 420 (1935).
27. D. Bitzer and H. J. Brielmaier, *Melliand Textilber.* **41**, 62 (1960).
28. J. Wegmann, *Melliand Textilber.* **39**, 408 (1958).
29. E. D. Owen and R. T. Allen, *J. Appl. Chem. Biotechnol.* **22**, 799 (1972).
30. C. H. Giles, C. D. Shah, W. E. Watts, and R. S. Sinclair, *J. Soc. Dyers Colour.* **88**, 433 (1972).
31. N. A. Evans and I. W. Stapleton, *J. Soc. Dyers Colour.* **89**, 208 (1973).
32. H. Obata, Y. Usui, and M. Koizumi, *Bull. Chem. Soc. Jpn.* **34**, 1049 (1961).
33. N. A. Evans, *J. Soc. Dyers Colour.* **89**, 332 (1973).
34. C. H. Giles and R. S. Sinclair, *J. Soc. Dyers Colour.* **88**, 109 (1972).
35. W. Herbst and K. Hunger, *Industrial Organic Pigments, Production, Properties, Applications*, VCH, Weinheim, Germany, 1993, 521–546.
36. Ger. Pat. 2,138,931 (Aug. 4, 1971), H. Kast, H. Baumann, U. Mayer, and A. Oberlinner (to BASF); see also U.S. Pat. 3,828,071.
37. Ger. Pat. 2,736,679 (Aug. 16, 1977), H. Kast and U. Mayer (to BASF); see also GB Pat. 2,003,096.
38. T. Sakakibara, J. Kotobuki, and Y. Dogomori, *Chem. Letts.*, 25 (1977).
39. Jpn. Pat. 56,057,848 (May 20, 1981), K. Takeo, S. Nobuo, and Y. Hiroyoshi (to Hodogaya Chemical Co).
40. U.S. Pat. 4,321,207 (Mar. 23, 1982), F. F. Cesark (to American Cyanamid).
41. U.S. Pat. 4,330,476 (May 18, 1982), K. H. Hermann (to Bayer).
42. U.S. Pat. 4,477,381 (Oct. 16, 1984), U. Mayer, E. Hahn, and J. Jesse (to BASF).
43. U.S. Pat. 4,566,999 (Jan. 28, 1986), A. Engelmann (to Hoechst and Cassella).
44. U.S. Pat. 4,678,613 (July 7, 1987), R. J. Flores (to PMC Specialties Group Inc.).
45. U.S. Pat. 4,824,610 (Apr. 25, 1989), R. J. Sappok, L. R. de Alvare, and F. G. Spence (to BASF).
46. U.S. Pat. 5,013,857 (May 7, 1991), H. Berneth and R. Raue (to Bayer).
47. U.S. Pat. 5,198,558 (Mar. 30, 1993), S. P. Rines and C. J. Zullig (to BASF).
48. Jpn. Pat. 2,194,188 (July 31, 1990), T. Aizawa (to Nippon Kayaku KK).
49. U.S. Pat. 4,775,451 (Oct. 4, 1988), W. Habermann, U. Mayer, P. Hammes, and B. Landmann (to BASF).
50. Ger. Pat. 2,152,703 (Oct. 22, 1971), H. Kast, H. Baumann, U. Mayer, and A. Oberlinner (to BASF); see also U.S. Pat. 3,828,071.
51. Ger. Pat. 1,098,652 (Feb. 2, 1961), G. Schafer and F. Quint (to Hoechst).
52. Ger. Pat. 2,753,072 (Nov. 29, 1977), M. Haehnke and E. Mundlos (to Hoechst).
53. E. Fox, ed., *Amer. Dystuff Rep.*, 141–154 (1992).
54. J. J.-P. Drake, *Toxicology* **5**, 3 (1975).
55. R. D. Combes and R. B. Haveland-Smith, *Mutat. Res.* **98**, 101–248 (1982).
56. S. Clemmensen, J. C. Jensen, N. J. Jensen, O. Meyer, P. Olsen, and G. Wurtzen, *Arch. Toxicol.* **56**, 43 (1984).
57. MAFF (1979), Interim Report on the Review of the Colouring Matter in Food Regulations, FAC/REP/29, Ministry of Agriculture, Fisheries and Food, Food Additives and Contaminants Committee, HMSO, London, 1973.
58. T. Gadian, *Rev. Prog. Coloration* **7**, 85 (1976).
59. E. A. Clarke and R. Anliker, *Rev. Prog. Coloration* **14**, 84 (1984). M. L. Richardson and A. Waggott, *Ecotoxicol. Environmental Safety* **5**, 424 (1981).
60. Dyes and the Environment, ADMI Reports on Selected Dyes and their Effects, Vol. 1 (Sept. 1973) and Vol. 2 (Sept. 1974), American Dye Manufacturers Institute.
61. J. E. Gwinn and D. C. Bomberger, *Wastes from Manufacture of Dyes and Pigments, Vol. 5: Diphenylmethane and Triarylmethane Dyes and Pigments*, Report No. EPA-600/2-84-111E, SRI International, Menlo Park, Calif., 1984.
62. I. G. Laing, *Rev. Prog. Coloration* **21**, 56 (1991).
63. C. Yatome, T. Ogawa, and E. Idaka, *Sen-I Gakkaishi* **40**, T344 (1984).

64. V. V. Solodovnikov, V. M. Zadorskii, G. P. Fedorchenko, and Z. I. Selemeneva, *Vopr. Khim. Khim. Tekhnol.* **72**, 117 (1983).
65. Ger. Pat. 3,641,525 (Dec. 5, 1986), H.-T. Macholdt and A. Sieber (to Hoechst); see also U.S. Pat. 5,061,585.
66. U.S. Pat. 4,832,992 (May 23, 1989), M. Yabe and Y. Inagaki (to Fuji Photo Film KK).
67. E. Akgun and M. Tunali, *Arch. Pharm.* **321**, 921 (1988).
68. C. de Diego, C. Avendano, and J. Elguero, *Chem. Scr.* **28**, 403 (1988).
69. R. Naef, *Dyes Pigm.* **6**, 233 (1985).
70. U.S. Pat. 4,720,449 (Jan. 19, 1988), A. L. Borror and E. W. Ellis (to Polaroid Corp.).
71. U.S. Pat. 5,028,725 (July 2, 1991), P. F. King (to Polaroid Corp.).
72. U.S. Pat. 5,094,688 (Mar. 10, 1992), U. Eckstein, H. Psaar, and G. Jabs (to Bayer).
73. U.S. Pat. 5,233,048 (Aug. 3, 1993), U. Eckstein and R. Raue (to Bayer).
74. M. Sumitana, *Kagaku Kogyo*, 379 (1986).
75. S. Akiyama, S. Nakatsuji, K. Nakashima, and M. Watanabe, *J. Chem. Soc., Chem. Commun.*, 710 (1987); S. Akiyama, S. Nakatsuji, K. Nakashima, and S. Yamasaki, *Dyes Pigm.* **9**, 459 (1988).
76. S. Akiyama, S. Nakatsuji, K. Nakashima, M. Watanabe, and H. Nakazumi, *J. Chem. Soc., Perkin Trans. I*, 3155 (1988); S. Nakatsuji, K. Nakashima, S. Akiyama, and H. Nakazumi, *Dyes Pigm.* **24**, 37 (1994).
77. U.K. Pat. 2,173,914 (Oct. 22, 1986), P. F. Gordon (to ICI).
78. Jpn. Pat. 63,226,667 (Sept. 21, 1988), J. Yamada and T. Baba (to Mitsubishi Paper Mills).

General References

79. D. R. Waring and G. Hallas, eds., *The Chemistry and Applications of Dyes*, Plenum Publishing Corp., New York, 1990.
80. P. Gregory, *High-Technology Applications of Organic Colorants*, Plenum Publishing Corp., New York, 1990.
81. G. Booth, *The Manufacture of Organic Colorants and Intermediates*, The Society of Dyers and Colourists, Bradford, U.K., 1988.
82. P. F. Gordon, P. Gregory, *Organic Chemistry in Colour*, Springer-Verlag, Berlin, 1983.
83. G. Hallas, in J. Shore, ed., *Colorants and Auxiliaries*, Vol. **1**, The Society of Dyers and Colourists, Bradford, U.K., 1990, 279–294.
84. E. N. Abrahart, *Dyes and their Intermediates*, 2nd ed., Chemical Publishing, New York, 1977.
85. R. L. M. Allen, *Color Chemistry*, Appleton-Century-Crofts, New York, 1971.
86. K. Ventkataraman, ed., *The Chemistry of Synthetic Dyes*, Vol. **2**, Academic Press Inc., New York, 1952; N. R. Ayyanger and B. D. Tilak, and D. R. Baer in Vol. **4**, 1971; J. Lenoir in Vol. **5**, 1971; E. Gurr, N. Anand, M. K. Unni, and N. R. Ayyanger in Vol. **7**, 1974; N. A. Evans and I. W. Stapleton in Vol. **8**, 1978.
87. P. Bentley and co-workers, *Review in Progress of Color and Related Topics*, Vol. **5**, The Society of Dyers and Colourists, Bradford, U.K., 1974.
88. Manufacture of Triphenylmethane Dyestuffs and Intermediates at Ludwigshafen and Hoechst, BIOS Final Report 959 (1945); Manufacture of Triphenylmethane Dyestuffs at Hoechst, Ludwigshafen, and Leverkusen, BIOS Final Report 1433, British Intelligence Objectives Subcommittee (1946); German Dyestuffs and Dyestuff Intermediates (Field Information Agency, Technical, FIAT) Final Report 1313 (1946).
89. *Colour Index*, 3rd ed., The Society of Dyers and Colourists, Bradford, U.K. and the American Association of Textile Chemists and Colorists, Research Triangle Park, N.C., Vols. **1–6**, 1971.
90. P. Rys and H. Zollinger, *Fundamentals of the Chemistry and Applications of Dyes*, Wiley-Interscience, New York, 1972.
91. H. A. Lubs, ed., *The Chemistry of Synthetic Dyes and Pigments*, American Chemical Society Monograph Series, Reinhold Publishing Corp., New York, 1955.
92. K. Venkataraman, ed., *The Analytical Chemistry of Synthetic Dyes*, Wiley-Interscience, New York, 1977.
93. J. Fabian and H. Hartmann, *Light Absorption of Organic Colorants*, Springer-Verlag, Berlin, 1980.
94. T. E. Furia, ed., *Handbook of Food Additives*, 2nd ed., CRC Press, Cleveland, Ohio, 1972.
95. D. M. Marmion, *Handbook of U.S. Colorants for Food, Drugs, and Cosmetics*, John Wiley & Sons, New York, 1979.
96. E. A. Clarke and R. Anliker, in O. Hutzinger, ed., *The Handbook of Environmental Chemistry*, Vol. **3**, Part A, 181–215, Springer-Verlag, Berlin, 1980.

97. E. Gurr, *Synthetic Dyes in Biology, Medicine and Chemistry*, Academic Press, London, 1971.
98. O. Valcl, I. Nemcova, and V. Suk, *Handbook of Triarylmethane and Xanthene Dyes: Spectrophotometric Determination of Metals*, CRC Press, Inc., Boca Raton, Fla., 1985.

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