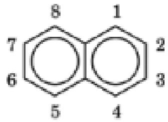
Kirk-Othmer Encyclopedia of Chemical Technology.

NAPHTHALENE DERIVATIVES

Naphthalene derivatives are of diverse importance as intermediates for agricultural, construction, pharmaceutical, photographic, rubber, tanning, and textile chemicals. In this article production figures, economics, and processes are discussed for most commercially important compounds. Sources for a more comprehensive study of naphthalene derivatives are available (1–8).

Several systems of nomenclature have been used for naphthalene, and many trivial and trade names are well established. The *Chemical Abstracts Index Guide* is employed in this article. The numbering of the naphthalene nucleus is shown in **(1)**; older practices are given in **(2)** and **(3)**.



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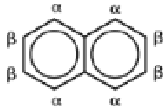

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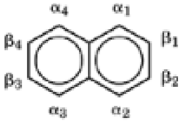

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Substituents in the 1,8 or 2,6 positions of naphthalene are in the peri or amphi positions, respectively.

The number of naphthalene derivatives is very large, since the number of positional isomers is large: 2 for monosubstitution, 10 for disubstitution–same substituent, 14 for disubstitition–different substituents, 14 for trisubstitution–same substituent, 42 for trisubstitution–two different substituents, 84 for trisubstitution–three different substituents, and so on with multiplying complexity.

1. Naphthalenesulfonic Acids

Naphthalenesulfonic acids are important chemical precursors for dye intermediates, wetting agents and dispersants, naphthols, and air-entrainment agents for concrete. The production of many intermediates used for making azo, azoic, and triphenylmethane dyes (qv) involves naphthalene sulfonation and one or more unit operations, eg, caustic fusion, nitration, reduction, or amination.

Commercially, sulfonation is carried out by the classic method with sulfuric acid. Modern reactors are glass-lined; older equipment was made from cast iron or coated with enamel. Processes often use chlorosulfonic acid or sulfur trioxide to minimize the need of excess sulfuric acid. Improved analytical methods have contributed to the success of process optimization (9–12).

Generally, the sulfonation of naphthalene leads to a mixture of products. Naphthalene sulfonation at less than ca 100°C is kinetically controlled and produces predominantly 1-naphthalenesulfonic acid 1. Sulfonation of naphthalene at above ca 150°C provides thermodynamic control of the reaction and 2-naphthalenesulfonic acid as the main product. Reaction conditions for the sulfonation of naphthalene to yield desired products are given in Figure 1; alternative paths are possible. A list of naphthalenesulfonic acids and some of their properties is given in Table 1.

1.1. 1-Naphthalenesulfonic Acid

The sulfonation of naphthalene with excess 96 wt % sulfuric acid at $<$ 80°C gives $>$ 85 wt % 1-naphthalenesulfonic acid (α -acid); the balance is mainly the 2-isomer (β-acid). An older German commercial process is based on the reaction of naphthalene with 96 wt % sulfuric acid at 20–50°C (13). The product can be used unpurified to make dyestuff intermediates by nitration or can be sulfonated further. The sodium salt of 1-naphthalenesulfonic acid is required, for example, for the conversion of 1-naphthalenol (1-naphthol) by caustic fusion. In this case, the excess sulfuric acid first is separated by the addition of lime and is filtered to remove the insoluble calcium sulfate; the filtrate is treated with sodium carbonate to precipitate calcium carbonate and leave the sodium 1-naphthalenesulfonate[130-14-3] in solution. The dry salt then is recovered, typically, by spray-drying the solution.

The older methods have been replaced by methods which require less, if any, excess sulfuric acid. For example, sulfonation of naphthalene can be carried out in tetrachloroethane solution with the stoichiometric amount of sulfur trioxide at no greater than 30°C, followed by separation of the precipitated 1-naphthalenesulfonic acid; the filtrate can be reused as the solvent for the next batch (14). The purification of 1-naphthalenesulfonic acid by extraction or washing the cake with 2,6-dimethyl-4-heptanone (diisobutyl ketone) or a C-1–4 alcohol has been described (15, 16). The selective insoluble salt formation of 1-naphthalenesulfonic acid in the sulfonation mixture with 2,3-dimethylaniline has been patented (17).

1-Naphthalenesulfonic acid can be converted to 1-naphthalenethiol[529-36-2] by reduction of the related sulfonyl chloride; this product has some utility as a dye intermediate, and is converted by reaction with alkyl isocyanates to *S*-naphthyl-*N*-alkylthiocarbamates, which have pesticidal and herbicidal activity (see Herbicides; Pesticides) (18). Either 1- or 2-naphthalenethiol reacts with acetic anhydride in the presence of sulfuric acid to produce naphthalene thioesters, used as substrates for a continuous, nondestructive kinetic assay of esterases associated with insecticide resistance (19).

1.2. 2-Naphthalenesulfonic Acid

The standard manufacture of 2-naphthalenesulfonic acid involves the batch reaction of naphthalene with 96 wt % sulfuric acid at ca 160°C for ca 2 h (13). The product contains the 1- and 2-isomers in a ratio of ca 15:85. Because of its faster rate of desulfonation, 1-naphthalenesulfonic acid can be hydrolyzed selectively by dilution

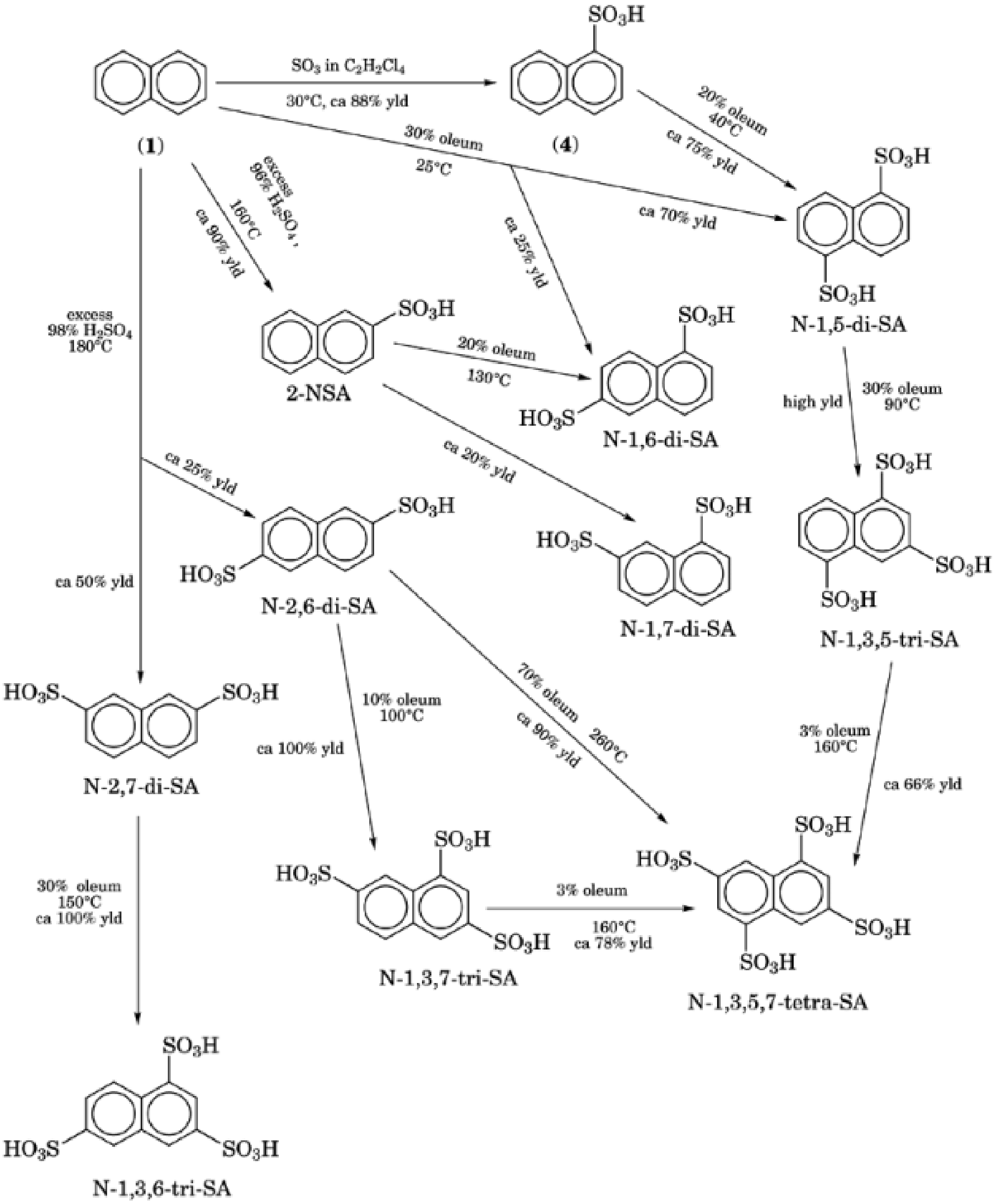


Fig. 1. Selected paths to naphthalenesulfonic acids where N = naphthalene, SA = sulfonic acid, and yld = yield.

of the charge with water and agitating for 1 h at 150°C; the naphthalene that is formed can be removed by steam distillation.

Sulfonation can be conducted with naphthalene–92 wt % H_2SO_4 in a 1:1.1 mole ratio with staged acid addition at 160°C over 2.5 h to give a 93% yield of the desired product (20). Continuous monosulfonation of naphthalene with 96 wt % sulfuric acid in a cascade reactor at ca 160°C gives 2-naphthalenesulfonic acid and

Table 1. Melting Points of Naphthalenesulfonic Acids

Compound	CAS Registry Number	Mp, °C	Mp of corresponding sulfonyl chloride, °C
1-naphthalenesulfonic acid	[85-47-2]	139–140	68
1-naphthalenesulfonic acid dihydrate	[6036-48-2]	90	
2-naphthalenesulfonic acid	[120-18-3]	139–140	76
2-naphthalenesulfonic acid hydrate	[76530-12-6]	124–125	
2-naphthalenesulfonic acid trihydrate	[17558-84-8]	83	
1,2-naphthalenedisulfonic acid	[25167-78-6]		160
1,3-naphthalenedisulfonic acid	[6094-26-4]		137.5
1,4-naphthalenedisulfonic acid	[46859-22-7]	240–245 dec	162
1,5-naphthalenedisulfonic acid	[81-04-9]	125 dec	183
1,6-naphthalenedisulfonic acid	[525-37-1]		129
1,7-naphthalenedisulfonic acid	[5724-16-3]		123
2,6-naphthalenedisulfonic acid	[581-75-9]	199 dec	228–229
2,7-naphthalenedisulfonic acid	[92-41-1]		159.5
1,3,5-naphthalenetrisulfonic acid	[6654-64-4]		146
1,3,6-naphthalenetrisulfonic acid	[86-66-8]		194–197
1,3,7-naphthalenetrisulfonic acid	[85-49-4]		165–166
1,4,5-naphthalenetrisulfonic acid	[60913-37-3]		156–157
1,3,5,7-naphthalenetetra-sulfonic acid	[6654-67-7]		261–262

small amounts of by-product naphthalenedisulfonic acids (21). The purification of 2-naphthalenesulfonic acid by hydrolysis of the 1-isomer can be done in a continuous manner (22, 23).

In the manufacture of 2-naphthalenol, 2-naphthalenesulfonic acid must be converted to its sodium salt; this can be done by adding sodium chloride to the acid, and by neutralizing with aqueous sodium hydroxide or neutralizing with the sodium sulfite by-product obtained in the caustic fusion of the sulfonate. The crude sulfonation product, without isolation or purification of 2-naphthalenesulfonic acid, is used to make 1,6-, 2,6-, and 2,7-naphthalenedisulfonic acids and 1,3,6-naphthalenetrisulfonic acid by further sulfonation. By nitration, 5- and 8-nitro-2-naphthalenesulfonic acids, [89-69-1] and [117-41-9], respectively, are obtained, which are intermediates for Cleve's acid. All are dye intermediates. The crude sulfonation product can be condensed with formaldehyde or alcohols or olefins to make valuable wetting, dispersing, and tanning agents.

1.3. 1,5- and 1,6-Naphthalenedisulfonic Acid

1,5- and 1,6-Naphthalenedisulfonic acids are co-products in the low temperature disulfonation of naphthalene. They are known by the trivial names Armstrong acid (1, 5) and Eiver-Pick acid (1, 6). A typical process involves the sulfonation of naphthalene with an excess of 20–30 wt % oleum at not over 25°C (24). The sulfonation mass is diluted with water, and the sodium salt of the disulfonic acid is formed by reaction with sodium sulfate. On cooling, the dihydrate of the disodium 1,5-naphthalenedisulfonate[76758-30-0] precipitates (ca 70% yield) and is recovered by filtration or centrifugation. The filtrate contains sodium 1,6-naphthalenedisulfonate[1655-43-2] which can be recovered by lime addition to precipitate sulfate as calcium sulfate and by filtration and evaporation of the filtrate. The sulfonation of naphthalene at -5 to 40°C in a chlorinated alkane solvent with SO_3 or first with chlorosulfonic acid, followed by sulfur trioxide, gives 1,5-naphthalenedisulfonic acid in excellent yields and purity (25).

1.4. 2,6- and 2,7-Naphthalenedisulfonic Acids

2,6-Naphthalenedisulfonic acid (Ebert-Merzβ-acid) is an important isomer and is useful as an intermediate for 2,6-naphthalenediol and as an additive for cleansing cosmetics (qv). The sulfonation of naphthalene with excess 98 wt % sulfuric acid at 135–180°C gives a mixture of 2,6- and 2,7-naphthalenedisulfonic acids; the mixture is diluted with water and converted to the sodium salt by the addition of NaCl or Na_2SO_4 (13). At first, sodium 2,6-naphthalenedisulfonate[1655-45-4] precipitates and is recovered by filtration in ca 25% yield; further salt addition and cooling precipitates sodium 2,7-naphthalenedisulfonate[1655-35-2] in ca 50% yield.

A naphthalene sulfonation product that is rich in the 2,6-isomer and low in sulfuric acid is formed by the reaction of naphthalene with excess sulfuric acid at 125°C and by passing the resultant solution through a continuous wiped-film evaporator at 245°C at 400 Pa (3 mm Hg) (26). The separation in high yield of 99% pure 2,6-naphthalenedisulfonate, as its anilinium salt from a crude sulfonation product, has been claimed (27). A process has been patented for the separation of 2,6-naphthalenedisulfonic acid from its isomers by treatment with phenylenediamine (28).

2,7-Naphthalenedisulfonic acid (Ebert-Merz α-acid) is partially isomerized in sulfuric acid at 160°C to 2,6-naphthalenedisulfonic acid. The reaction takes place by a desulfonation–resulfonation mechanism.

1.5. 1,3,5- and 1,3,6-Naphthalenetrisulfonic Acids

The sulfonation of 1,5-naphthalenedisulfonic acid with oleum at 90°C gives 1,3,5-naphthalenetrisulfonic acid in good yield (29). 1,3,6-Naphthalenetrisulfonic acid can be made by sulfonation of 1,6- or 2,7-naphthalenedisulfonic acid but this is a fairly costly process (30). A more acceptable manufacturing method involves the time– temperature–acid concentration-programmed sulfonation of naphthalene with sulfuric acid and oleum (31).

1.6. Alkylnaphthalenesulfonic Acids

The alkylnaphthalenesulfonic acids can be made by sulfonation of alkylnaphthalenes, eg, with sulfuric acid at 160°C, or by alkylation of naphthalenesulfonic acids with alcohols or olefins. These products, as the acids or their sodium salts, are commercially important as textile auxiliaries, surfactants (qv), wetting agents, dispersants (qv), and emulsifying aids, eg, for dyes (qv), wettable powder pesticides, tars, clays (qv), and hydrotropes.

1.7. Naphthalenesulfonic Acid–Formaldehyde Condensates

The sodium salts of the condensation products of naphthalenesulfonic acid with formaldehyde constitute an important class of compounds which are mainly used in the area of concrete additives (32, 33), agricultural formulations, rubber formulations, and synthetic tanning agents. They are also used in photographic materials (34). Hampshire Chemical Co. and Henkel of America, Inc., are the largest suppliers of naphthalene sulfonate in concrete additives (superplasticizer) and reportedly hold 75–80% of this market. It was estimated that naphthalene sulfonate demand from U.S. producers would reach approximately

$$15 \times 10^3\ \mathrm{t/yr}$$

for all surfactant and dispersant applications by 1994, representing an average annual growth rate of approximately 5%; most of the demand is from the growth of naphthalene sulfonate formaldehydes (35). In addition, the domestic consumption of naphthalene sulfonate syntans for leather tanning was estimated to be more than

$$7 \times 10^3\ \mathrm{t/yr}$$

Table 2. Melting Point of Nitronaphthalenes

Compound	CAS Registry Number	Mp, °C
1-nitronaphthalene	[86-57-7]	52[a]; 57.8[b]
2-nitronaphthalene[c]	[581-89-5]	78.7[d]
1,2-dinitronaphthalene[c]	[24934-47-2]	161–162
1,3-dinitronaphthalene[c]	[606-37-1]	148
1,4-dinitronaphthalene[c]	[6921-26-2]	134
1,5-dinitronaphthalene	[605-71-0]	219
1,6-dinitronaphthalene[c]	[607-46-5]	166.5[e]
1,7-dinitronaphthalene[c]	[24824-25-7]	156
1,8-dinitronaphthalene	[602-38-0]	172
2,3-dinitronaphthalene[c]	[1875-63-4]	174.5–175
2,6-dinitronaphthalene[c]	[24824-26-8]	279
2,7-dinitronaphthalene[c]	[24824-27-9]	234
1,2,3-trinitronaphthalene[c]	[76530-13-7]	190
1,2,4-trinitronaphthalene[c]	[76530-14-8]	258
1,3,5-trinitronaphthalene	[2243-94-9]	122
1,3,6-trinitronaphthalene[c]	[59054-75-0]	186
1,3,8-trinitronaphthalene	[2364-46-7]	218
1,4,5-trinitronaphthalene	[2243-95-0]	149
1,3,5,7-tetranitronaphthalene[c]	[60619-96-7]	260
1,3,5,8-tetranitronaphthalene	[2217-58-5]	194–195
1,3,6,8-tetranitronaphthalene	[28995-89-3]	203
1,4,5,8-tetranitronaphthalene	[4793-98-0]	340–345 dec

[a] Metastable form.
[b] Bp 304°C (169°C at 1.6 kPa (12 mm Hg)).
[c] Made by indirect methods, not by the direct nitration of naphthalene or naphthalene-nitration products.
[d] Bp 312.5°C at 97.8 kPa (733 mm Hg) and 165°C at 2.0 kPa (15 mm Hg).
[e] Bp 370°C (235°C at 1.3 kPa (9.75 mm Hg)).

In 1994 estimated naphthalene consumption in western Europe and Japan for the production of alkylnaphthalene sulfonates, naphthalene sulfonate formaldehyde condensates, and synthetic tanning agents was

$$34 \times 10^3$$

and

$$17 \times 10^3 \text{ t/yr}$$

, respectively. G. Bozzetto (Italy), part of the Ruetgers Werke group, produces about

$$15 \times 10^3 \text{ t/yr}$$

of naphthalene sulfonate condensates (35).

1.8. Hydronaphthalenesulfonic Acid

Sodium tetralinsulfonate[37837-69-7] (sodium 1,2,3,4-tetrahydronaphthalenesulfonate) is marketed by Du Pont as a dispersing and solubilizing agent under the trade name Alkanol S. Poly(dihydronaphthalene) sulfonates have been proposed for use as ion-exchange resins and antistatic agents for thermoplastics (36).

2. Nitronaphthalenes and Nitronaphthalenesulfonic Acids

The nitro group does not undergo migration of the naphthalene ring during the usual nitration procedures. Therefore, mono- and polynitration of naphthalene is similar to low temperature sulfonation. The nitronaphthalenes and some of their physical properties are listed in Table 2. Many of these compounds are not accessible by direct nitration of naphthalene but are made by indirect methods, eg, nitrite displacement of diazonium halide groups in the presence of a copper catalyst, decarboxylation of nitronaphthalenecarboxylic acids, or deamination of nitronaphthalene amines.

2.1. 1-Nitronaphthalene

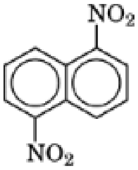
1-Nitronaphthalene is manufactured by nitrating naphthalene with nitric and sulfuric acids at ca 40–50°C (37). The product is obtained in very high yield and contains ca 3–10 wt % 2-nitronaphthalene and traces of dinitronaphthalene; the product can be purified by distillation or by recrystallization from alcohol. 1-Nitronaphthalene is important for the manufacture of 1-naphthaleneamine. Photochemical nitration of naphthalene by tetranitromethane in dichloromethane and acetonitrile to give 1-nitronaphthalene has been described (38).

2-Nitronaphthalene is metabolized to the carcinogenic 2-naphthylamine in the human body (39). Respirators, protective clothing, proper engineering controls, and medical monitoring programs for workers involved in making by-product 2-nitronaphthalene should be used.

2.2. 1,5- and 1,8-Dinitronaphthalenes

1,5- and 1,8-dinitronaphthalenes, **(5)** and **(6)**, respectively, can be made by nitration of 1-nitronaphthalene in a ∼ 40:60 ratio. Similar results are obtained by the direct dinitration of naphthalene with mixed acid at 40–80°C and separation of isomers by fractional crystallization from ethylene dichloride (13). Process studies involve improvements in the separation of 1,5- and 1,8-dinitronaphthalenes by solvent extraction (40). The analysis of the mono- and dinitronaphthalenes can be done by gas–liquid chromatography (glc).

The reaction of the corresponding diamine of 1,5-dinitronaphthalene with phosgene produces 1,5-naphthalenediisocyanate[3173-72-6] (41, 42). 1,8-Dinitronaphthalene is reduced to 1,8-diaminonaphthalene, which is an intermediate for making phthaloperinone[6925-69-5] **(7)**, an orange colorant for plastics.



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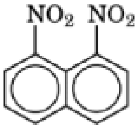

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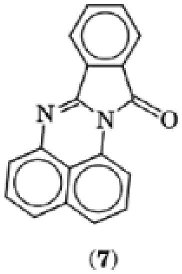

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2.3. Nitronaphthalenesulfonic Acids

Nitronaphthalenesulfonic acids can be obtained either by the sulfonation of 1-nitronaphthalene or by the nitration of 1- or 2-naphthalenesulfonic acid. Thus the sulfonation of 1-nitronaphthalene with oleum at ca 25°C gives mainly 5-nitro-1-naphthalenesulfonic acid[17521-00-5]. The mononitration of 1-naphthalenesulfonic acid gives mainly 5- and 8-nitro-1-naphthalenesulfonic acid[117-41-9] and mononitration of 2-naphthalenesulfonic acid gives mainly 5-nitro-2-naphthalenesulfonic acid [86-69-1] and 8-nitro-2-naphthalenesulfonic acid [18425-74-6]. These compounds seldom are isolated; usually, the nitro group is reduced to the amino group to obtain dye intermediates.

3. Naphthaleneamines and Naphthalenediamines

Selected physical properties of naphthaleneamines and naphthalenediamines are listed in Table 3.

3.1. 1-Naphthaleneamine

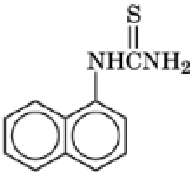
1-Naphthylamine or α-naphthylamine[139-32-7] can be made from 1-nitronaphthalene by reduction with iron–dilute HCl, or by catalytic hydrogenation; it is purified by distillation and the content of 2-naphthylamine can be reduced as low as 8–10 ppm. Electroreduction of 1-nitronaphthalene to 1-naphthylamine using titania–titanium composite electrode has been described (43). Photoinduced reduction of 1-nitronaphthalene on semiconductor (eg, anatase) particles produces 1-naphthylamine in 77% yield (44). 1-Naphthylamine[134-32-7] can also be prepared by treating 1-naphthol with NH_3 in the presence of a catalyst at elevated temperature. The sanitary working conditions are improved by gas-phase reaction at 200–450°C using a dehydration catalyst consisting of aluminosilicate, Al_2O_3, or silica gel (45). 1-Naphthaleneamine is also toxic (LD_{50} (dogs) = 400 mg/kg) and a suspected human carcinogen, which conditions mandate that appropriate precautions be followed in manufacture and use.

1-Naphthaleneamine is a dye intermediate and is used as the starting material in the manufacture of the rodenticide, Antu **(8)**, 1-naphthalenethiourea[86-88-4], which is prepared by heating a mixture of 1-naphthylamine hydrochloride, NH_4SCN, and a large amount water for 14–16 h while keeping its volume constant by adding an additional amount of water, to give a 97% yield. Its LD_{50} is 600 mg in squirrels (46).

Table 3. Physical Properties of Naphthaleneamines and Naphthalenediamines

Compound	CAS Registry Number	Mp, °C	Density	Other
1-naphthaleneamine	[134-32-7]	50	1.13^{14}_{4}	flash pt, 157°C; sol 0.496 g/L H_2O; vol with steam; bp 301°C (160°C at 1.6 kPa[a])
2-naphthaleneamine	[91-59-8]	111–113	1.061^{98}_{4}	sol hot water; vol with steam; bp 306°C (175.8°C at 2.7 kPa[a])
1,2-naphthalenediamine	[938-25-0]	96–98		sol hot water, alc, ether; bp at 0.01 kPa[a] 150–151°C
1,4-naphthalenediamine	[2243-61-0]	120		sl sol hot water
1,5-naphthalenediamine	[2243-62-1]	189.5		sol hot water, alc
1,6-naphthalenediamine	[2243-63-2]	78	$1.147^{99.4}_{4}$	sol hot water, alc
1,7-naphthalenediamine	[2243-64-3]	117.5		sol alc
1,8-naphthalenediamine	[479-27-6]	66.5	$1.127^{99.4}_{4}$	sol alc, ether; bp at 1.6 kPa[a] 205°C
2,3-naphthalenediamine	[771-97-1]	191		sol alc, ether
2,6-naphthalenediamine	[2243-67-6]	216–218		sparingly sol alc, ether
2,7-naphthalenediamine	[613-76-3]	159		

[a] To convert kPa to mm Hg, multiply by 7.5.



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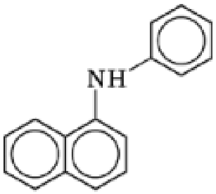

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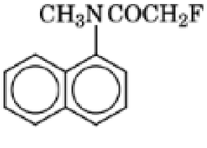

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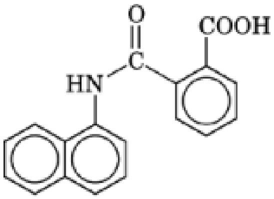
1-Naphthaleneamine is also the starting material for making the rubber antioxidant, *N*-phenyl-1-naphthaleneamine[90-30-2] **(9)**, made by the condensation of 1-naphthaleneamine or 1-naphthalenol with aniline. Fluoroacetamidonaphthalene [5903-13-9] (Nissol) **(10)**, an insecticide and miticide, is made from

1-naphthaleneamine by adding FCH_2COCl dropwise to a mixture of 1-*N*-methylnaphthylamine and benzene and refluxing for 2 h (47), or in an improved method, PCl_3 and $ClCH_2COOH$ are heated in xylene at 50–60°C to give $ClCH_2COCl$, which is treated with a solution of 1-naphthylamine in xylene 70–78°C and then at 100–120°C to give 92% *N*-1-naphthylchloroacetamide of 93% purity. *N*-1-Naphthylchloroacetamide is then methylated with $(CH_3)_2SO_4$ and fluorinated with KF to give 78–80% Nissol of 93–95% purity (48). The herbicide, Naptalam **(11)** Alanap,e or Dyanap, or *N*-1-naphthylphthalamic acid[132-66-1] is usually prepared by adding 1-naphthylamine to an aqueous slurry of phthalic anhydride. The yield of the product is about 96% (49).



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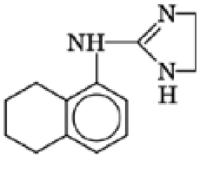

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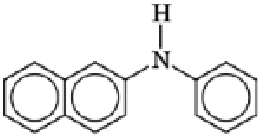
A tetrahydronaphthaleneamine derivative, 2-(5,6,7,8-tetrahydro-1-naphthaleneamine)-2-imidazoline **(12)**, is used in the hydrochloride form as an adrenergic agent, ie, tramazoline hydrocholoride, also called KB 227 and Rhinaspray.

3.2. 2-Naphthaleneamine

2-Naphthylamine or (PBNA) **(13)**, which is made by the condensation of 2-naphthol and with aniline in the presence of an acid catalyst. *N*-Phenyl-2-naphthaleneamine is metabolized in the human body to 2-naphthylamine; the National Institute of Occupational Safety and Health (NIOSH) has published recommendations for working with this product (36).

3.3. 1,5-Naphthalenediamine

1,5-Naphthylenediamine **(14)** is manufactured by metal-acid, eg, iron–acetic acid, reduction, or by catalytic hydrogenation of 1,5-dinitronaphthalene (50). Aside from its possible use as an intermediate for azo dyes, 1,5-naphthalenediamine is used for the manufacture of 1,5-naphthalene diisocyanate[3173-72-6] **(15)** by the phosgenation route. This diisocyanate is used for making high grade urethane cast elastomers.



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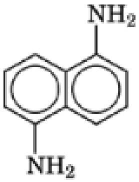

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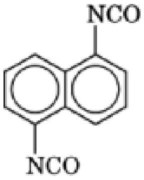

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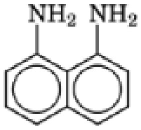

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3.4. 1,8-Naphthylenediamine

1,8-Naphthylenediamine **(16)** is produced by metal-acid reduction or by catalytic hydrogenation of 1,8-dinitronaphthalene (50). The most important use of 1,8-naphthylenediamine is for the manufacture, by condensation with phthalic anhydride, of phthaloperinone **(7)**, an orange colorant for plastics used in automobile turn-signal and warning-light lenses.

4. Aminonaphthalenesulfonic Acids

Many aminonaphthalenesulfonic acids are important in the manufacture of azo dyes (qv) or are used to make intermediates for azo acid dyes, direct, and fiber-reactive dyes (see Dyes, reactive). Usually, the aminonaphthalenesulfonic acids are made by either the sulfonation of naphthalenamines, the nitration–reduction of naphthalenesulfonic acids, the Bucherer-type amination of naphtholsulfonic acids, or the desulfonation of an aminonaphthalenedi- or trisulfonic acid. Most of these processes produce by-products or mixtures which often are separated in subsequent purification steps. A summary of commercially important aminonaphthalenesulfonic acids is given in Table 4.

Table 4. Manufacture, Production, and Application Data for Selected Aminonaphthalenesulfonic Acids

Acid	Trivial name	CAS Registry Number	Manufacturing method[a,eb,c,d]	Intermediate for
1-amino-2-naphthalenesulfonic		[81-06-1]	[a] or [e] using naphthionic acid	azo dyes, eg, CI Direct Violet 11
4-amino-2-naphthalenesulfonic		[134-54-3]	[d]	4-hydroxy-2-naphthalenesulfonic acid
4-amino-1-naphthalenesulfonic	Piria's acid; naphthionic acid	[84-86-6]	[a]	azo dyes, eg, CI Acid Red 88 and Acid Brown 14; 4-hydroxy-1-naphthalenesulfonic acid
5-amino-1-naphthalenesulfonic	Laurent's acid	[84-89-9]	[a] or [b] with Peri acid as the co-product	azo dyes, eg, CI Acid Black 24 and Mordant Brown 1; 5-hydroxy-1-naphthalenesulfonic acid; 5-amino-1,3-naphthalenedisulfonic acid; M-acid; 5-amino-1-naphthalenol
5-amino-2-naphthalenesulfonic	1,6-Cleve's acid	[119-79-9]	[b] with 1,7-Cleve's acid as the co-product	azo dyes, eg, CI Direct Blue 120; 5-amino-8-acet-amino-2-naphthalenesulfonic acid
8-amino-2-naphthalenesulfonic	1,7-Cleve's acid	[119-28-8]	[b] with 1,6-Cleve's acid	azo dyes, eg, CI Direct Green 51; 8-amino-2-naphthalenol; 4-amino-1,6-naphthalene-disulfonic acid
5- and 8-amino-2-naphthalenesulfonic	Cleve's acid (mixed)		[b]	azo dyes, eg, CI Direct Brown 62
8-amino-1-naphthalenesulfonic	Peri acid	[82-75-7]	[b] with Laurent's acid as the primary by-product	azo dyes, eg, CI Acid Black 35; 8-hydroxy-1-naphthalenesulfonic acid; 4-amino-1,5-naphthalenedisulfonic acid; 1,8-naphtho-sultam; 4-amino-1,3,5-naphthalene-trisulfonic acid
8-phenylamino-1-naphthalenesulfonic	Phenyl Peri acid	[82-76-8]	by condensation of aniline with Peri acid	azo dyes, eg, CI Acid Blue 113
2-amino-1-naphthalenesulfonic	Tobias acid	[81-16-3]	[c]	pigments, eg, CI Pigment Red 49; 6-amino-1-naphthalenesulfonic acid; 6-amino-1,3-naphthalenedisulfonic acid
6-amino-1-naphthalenesulfonic	Dahl's acid	[81-05-0]	[d] using Tobias acid	azo dyes, eg, CI Acid Green 12, one of six listed; 6-hydroxy-1-naphthalenesulfonic acid
6-amino-2-naphthalenesulfonic	Broenner's acid	[93-00-5]	[c]	azo dyes, eg, CI Direct Red 4
7-amino-2-naphthalenesulfonic	F-acid	[92-40-0]	[c]	azo dyes, eg, CI Direct Red 22
7-amino-1-naphthalenesulfonic	Badische acid	[86-60-2]	[c]	azo dyes, eg, CI Direct Green 33
1-amino-2,7-naphthalenedisulfonic	Kalle's acid	[486-54-4]	[d]	triphenylmethane dye
4-amino-2,7-naphthalenesulfonic	1,3,6-Freund's acid	[6521-07-6]	[b] with 1,3,7-Freund's acid	azo dyes, eg, CI Acid Black 7; 5-hydroxy-2,7-naphthalenedisulfonic acid
4-amino-2,6-naphthalenedisulfonic	1,3,7-Freund's acid	[6362-05-6]	[b] 1,3,6-Freund's acid is co-product	azo dyes, eg, CI Direct Orange 49
8-amino-1,6-naphthalenedisulfonic	amino-ϵ-acid	[129-91-9]	[b]	4-amino-2-naphthalenesulfonic acid; 8-hydroxy-1,6-naphthalenedisulfonic acid; 4-hydroxy-2-naphthalenesulfonic acid
4-amino-1,7-naphthalenedisulfoni	Dahl's acid II	[85-74-5]	[a] using naphth-ionic acid or 1,6-Cleve's acid	azo dyes, eg, CI Direct Orange 69

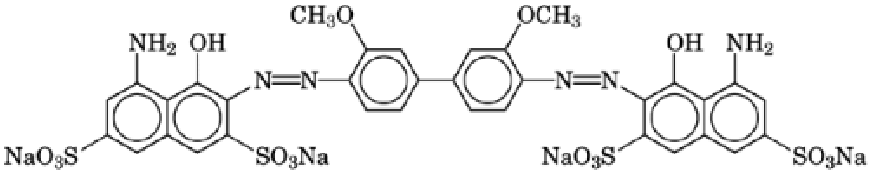
Table 4. ***Continued***

Acid	Trivial name	CAS Registry Number	Manufacturing method[a,eb,c,d]	Intermediate for
4-amino-1,6-naphthalenedisulfonic	Dahl's acid III	[85-75-6]	[a] as by-product of Dahl's acid II	azo dyes, eg, CI Direct Orange 49; 4-hydroxy-1,6-naphthalenedisulfonic acid
8-amino-1,5-naphthalenedisulfonic		[117-55-5]	[a] or [b]	8-hydroxy-1,5-naphthalenedisulfonic acid; 4-amino-5-hydroxy-1-naphthalenesulfonic acid
5-amino-1,3-naphthalenedisulfonic		[13306-42-8]	[d]	4-hydroxy-8-amino-2-naphthalenesulfonic acid
3-amino-2,7-naphthalenedisulfonic	amino-R-acid	[92-28-4]	[c]	azo dyes, eg, CI Direct Orange 13; 6-hydroxy-7-amino-2-naphthalenesulfonic acid
3-amino-1,5-naphthalenedisulfonic	Cassella acid	[131-27-1]	[b]	azo dyes, eg, CI Direct Red 15; 7-hydroxy-1,5-naphthalenedisulfonic acid
6-amino-1,3-naphthalenedisulfonic	amino J-acid	[118-33-2]	[d]	J-acid (3-hydroxy-6-amino-2-naphthalenesulfonic acid)
7-amino-1,3-naphthalenedisulfonic	amino G-acid	[86-65-7]	[c]	azo dyes, eg, CI Direct Orange 74; γ-acid (4-hydroxy-6-amino-2-naphthalenesulfonic acid)
4-amino-1,3,5-naphthalenetrisulfonic (as the sultam)		[76530-15-9]	[a]	Chicago acid (4-amino-5-hydroxy-1,3-naphthalene-disulfonic acid)
8-amino-1,3,6-naphthalenetrisulfonic	Koch's acid	[117-42-0]	[b]	H-acid; chromotropic acid; 8-hydroxy-1,3,6-naphthalenetrisulfonic acid
8-amino-1,3,5-naphthalenetrisulfonic	B-acid	[17894-99-4]	[b]	K-acid (4-amino-5-hydroxy-1,7-naphthalenedi-sulfonic acid)
6-amino-1,3,5-naphthalenetrisulfonic		[55524-4-0]	[a]	6-amino-1,3-naphthalenedisulfonic acid; -amino-5-2hydroxy-1,7-naphthalenedisulfonic acid
7-amino-1,3,6-naphthalenetrisulfonic	2R amino acid	[118-03-6]	[a]	3-amino-5-hydroxy-2,7-naphthalenedisulfonic acid
6,8-di(phenylamino)-1-naphthalene-sulfonic	diphenyl-ϵ-acid	[129-93-1]	from aniline and 8-amino-1,6-naphthalenedisulfonic acid	safranine dyes, eg, CI Acid Blue 61

[a] By sulfonation of the appropriate naphthaleneamine or aminonaphthalenesulfonic acid.
[b] By nitration/reduction of the appropriate naphthalene(poly)sulfonic acid.
[c] By amination of the appropriate hydroxynaphthalenesulfonic acid.
[d] By the desulfonation of an aminonaphthalenedi- or trisulfonic acid.
[e] By rearrangement of another aminonaphthalenesulfonic acid.

H-acid, 1-hydroxy-3,6,8-trisulfonic acid, which is one of the most important letter acids, is prepared as naphthalene is sulfonated with sulfuric acid to trisulfonic acid. The product is then nitrated and neutralized with lime to produce the calcium salt of 1-nitronaphthalene-3,6,8-trisulfonic acid, which is then reduced to T-acid (Koch acid) with Fe and HCl; modern processes use continuous catalytical hydrogenation with Ni catalyst. Hydrogenation has been performed in aqueous medium in the presence of Raney nickel or Raney

Ni–Fe catalyst with a low catalyst consumption and better yield (51). Fusion of the T-acid with sodium hydroxide and neutralization with sulfuric acid yields H-acid. Azo dyes such as Direct Blue 15 [2429-74-5] **(17)** and Acid Black[1064-48-8] **(18)** are the coupling products of H-acid (52).



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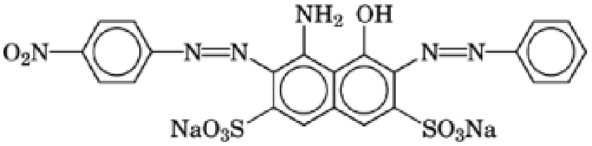

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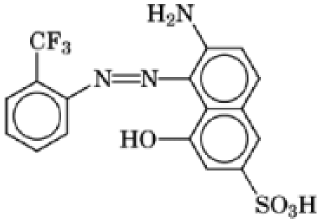

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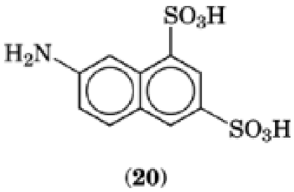
An example of an azo dyestuff in which γ-acid is the coupling component is Acid Red 337 **(19)**, which is obtained through the reaction of diazotized *o*-trifluoromethylaniline and γ-acid (52).

7-Amino-1,3-naphthalenedisulfonic acid **(20)** is made by the Bucherer amination route (53). A mixture of dipotassium 7-hydroxy-1,3-naphthalenedisulfonate[842-18-2], excess aqueous ammonia, and ammonium sulfite is heated slowly in an autoclave to 185°C and is maintained at this temperature for ca 16 h. Aqueous (50 wt %) sodium hydroxide is added to the charge to liberate ammonia, which is recovered for recycling. The charge is neutralized with a mineral acid. The yield of amino G-salt is 97% of theoretical yield. Ammoniation of the di-NH$_4$ salt of 7-hydroxy-1,3-naphthalenedisulfonic acid in the presence of sodium sulfite gives the 7-amino-1,3-naphthalenedisulfonic acid in increased purity and requires only one-fourth of the reaction time compared with the process starting from the di-K salt of 7-hydroxy-1,3-naphthalenedisulfonic acid (54).



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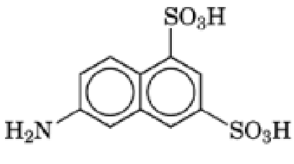

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Another example of manufacture in this series is the sulfonation of an aminonaphthalenesulfonic acid, followed by selected desulfonation, to make 6-amino-1,3-naphthalenedisulfonic acid **(21)**. Thus, 2-amino-1-naphthalenesulfonic acid made by amination of 2-hydroxy-1-naphthalenesulfonic acid is added to 20 wt % oleum at ca 35°C. At this temperature, 65 wt % oleum is added and the charge is stirred for 2 h, is then slowly heated to 100°C and is maintained for 12 h to produce 6-amino-1,3,5-naphthalenetrisulfonic acid. The mass is diluted with water and maintained for 3 h at 105°C to remove the sulfo group adjacent to the amino group. After cooling to ca 20°C and filtration, 6-amino-1,3-naphthalenedisulfonic acid is obtained in 80% yield (55).

5. Naphthalenols and Naphthalenediols

Naphthalenols, naphthalenediols, and their sulfonated and amino derivatives are important intermediates for dyes, agricultural chemicals, drugs, perfumes, and surfactants. The methods of manufacture include caustic fusion of naphthalene-1-sulfonic acid, hydrolysis of 1-chloro- or bromonaphthalene, pressure hydrolysis of 1-naphthaleneamine, oxidation–aromatization of tetralin, and hydroperoxidation of 2-isopropylnaphthalene[2027-17-0]. As the toxic hazard of the 1-naphthaleneamine was recognized, its commercial use was minimized. The sulfonation–caustic fusion process is more difficult to operate than in the past because of increasing difficulties posed by product purity requirements, high investment and replacement cost, and by-product effluent handling problems. In the United States, the naphthalenols are made by hydrocarbon oxidation routes.

The chemical properties of the naphthaleneols are similar to those of phenol and resorcinol, with added reactivity and complexity of substitution because of the condensed ring system. Some of the naphthols and naphthalenediols are listed with some of their physical properties in Table 5.

5.1. 1-Naphthalenol

1-Naphthol, α-naphthol, or 1-hydroxynaphthalene[90-15-3] forms colorless needles, mp 96°C, bp 288°C, which tend to become colored on exposure to air or light. It is almost insoluble in water, but readily soluble in alcohol, ether, and benzene. 1-Naphthol and 2-naphthol are found in coal tar (56).

Acid-catalyzed hydroxylation of naphthalene with 90% hydrogen peroxide gives either 1-naphthol or 2-naphthiol at a 98% yield, depending on the acidity of the system and the solvent used. In anhydrous hydrogen fluoride or 70% HF–30% pyridine solution at $-$ 10 to + 20°C, 1-naphthol is the product formed in $>$ 98% selectivity. In contrast, 2-naphthol is obtained in hydroxylation in super acid ($HF–BF_3$, $HF–SbF_5$, $HF–TaF_5$, $FSO_3H–SbF_5$) solution at $-$ 60 to $-$ 78°C in $>$ 98% selectivity (57). Of the three commercial methods of manufacture, the pressure hydrolysis of 1-naphthaleneamine with aqueous sulfuric acid at 180°C has been abandoned, at least in the United States. The caustic fusion of sodium 1-naphthalenesulfonate with 50 wt % aqueous sodium hydroxide at ca 290°C followed by the neutralization gives 1-naphthalenol in a ca 90% yield.

The most important process to produce 1-naphthalenol was developed by Union Carbide and subsequently sold to Rhône-Poulenc. It is the oxidation of tetralin, 1,2,3,4-tetrahydronaphthalene[119-64-2], in the presence of a transition-metal catalyst, presumably to 1-tetralol–1-tetralone by way of the 1-hydroperoxide, and dehydrogenation of the intermediate ie, 1-tetralol to 1-tetralone and aromatization of 1-tetralone to 1-naphthalenol,

Table 5. Properties of Naphthalenols and Naphthalenediols

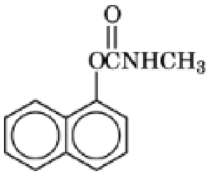
Compound	CAS Registry Number	Mp, °C	Density	Other
1-naphthalenol	[90-15-3]	95.8–96.0	$1.224^{4}_{4}1.099^{99}_{4}$	sublimes; sol 0.03 g/100 mL H_2O at 25°C; readily sol alc, ether, benzene; bp 280°C (158°C at 2.6 kPa[a])
2-naphthalenol	[135-19-3]	122	$1.078^{130}_{4}1.22^{25}_{4}$	sublimes; sol 0.075 g/100 mL H_2O at 25°C; readily sol alc, ether, benzene; flash pt 161°C; bp 295°C (161.8°C at 2.6 kPa[a])
1,2-naphthal-enediol	[574-00-5]	103–104		
1,3-naphthal-enediol	[132-86-5]	124		
1,4-naphthal-endiol	[571-60-8]	195		heat of combusion 4.77 MJ[b]
1,5-naphthal-enediol	[83-56-7]	258		sublimes; sparingly sol water; readily sol ether, acetone
1,6-naphthal-enediol	[575-44-0]	137–138		
1,7-naphthal-enediol	[575-38-2]	181		
1,8-naphthal-enediol	[569-42-6]	144		
2,3-naphthal-enediol	[92-44-4]	159		
2,6-naphthal-enediol	[581-43-1]	222		
2,7-naphthal-enediol	[582-17-2]	194		sol boiling water

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert MJ to kcal, divide by 4.184×10^{-3}.

using a noble-metal catalyst (58). 1-Naphthol production in the Western world is around 15×10^3 t/yr, with the United States as the largest producer (52).

1-Naphthol is mainly used in the manufacture of the insecticide carbaryl (59), 1-naphthyl *N*-methylcarbamate[63-25-2] (Sevin) **(22)**, which is produced by the reaction of 1-naphthol with methyl isocyanate. Methyl isocyanate is usually prepared by treating methylamine with phosgene. Methyl isocyanate is a very toxic liquid, boiling at 38°C, and should not be stored for long periods of time (Bhopal accident, India). India has developed a process for the preparation of aryl esters of *N*-alkyl carbamic acids. Thus 1-naphthyl methylcarbamate is prepared by refluxing 1-naphthol with ethyl methylcarbamate and $POCl_3$ in toluene (60). In 1992, carbaryl production totaled $> 11.4 \times 10^3$ t (35). Rhône-Poulenc, at its Institute, W. Va., facility is the only carbaryl producer in United States.

Devrinol, 2-(1-naphthoxy)-*N,N*-diethylpropionamide[16299-99-7] (napropamide) **(23)**, which is prepared from 1-naphthol, is used as a herbicide (61). Another agricultural chemical, 1-naphthoxyacetic acid[2976-75-2] **(24)**, is prepared by stirring 1-naphthol with monochloroacetic acid and sodium hydroxide in water at 100–110°C for several minutes. After treatment with concentrated HCl about 94% of the product is obtained (62).



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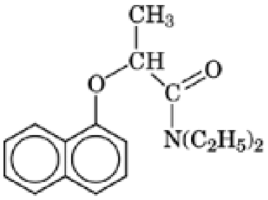

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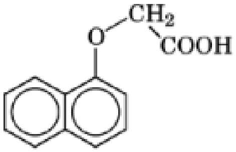

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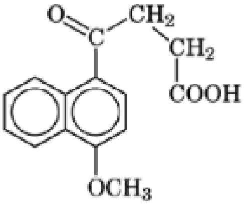
Several biologically and pharmacologically active compounds have been prepared from the condensation of the acid chloride of 1-naphthoxyacetic acid with carbazole, indole, or pyrrole in 2*N* NaOH solution in ethanol (63). Also, naphthyloxy derivatives of imidazole, benzimidazole, and benzotriazoles have been synthesized and screened for their antimicrobial, analgesic, and antiinflammatory activities. 2-Naphthyloxy derivatives are comparatively more active than 1-naphthyloxy derivatives (64).

Several drugs are derived from 1-naphthalenol: the magnesium salt of 3-(4-methoxy-1-naphthoyl)propionic acid[6643-66-6] (Hepalande) **(25)** is used as a choleretic (65). Propranolol (Inderal), 1-isopropylamino-3-(1-naphthoxy)-2-propanol[3506-09-0] **(26)**, is an important adrenergic blocking agent used in the treatment of angina and cardiac arrhythmias, with a worldwide production of approximately 500 t/yr (52). It is prepared by the reaction of 1-naphthol with epichlorohydrin, followed by substitution of the chlorine in 1-chloro-3-(1-naphthoxy)-2-propanol with isopropylamine (66). 1-Naphthyl salicylate[550-97-0] (Alphol) **(27)** has been used as an antiseptic and antirheumatic and is prepared by the acylation of phenols with salicylic acid using polyphosphoric acid (67).



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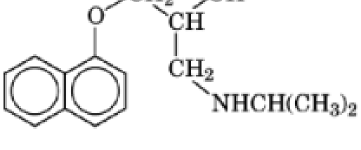

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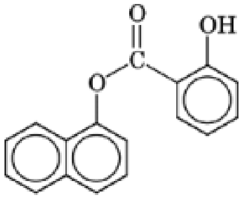

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1-Naphthalenol also is used in the preparation of azo, indigoid, and nitro, eg, 2,4-dinitro-1-naphthol, dyes, and in making dye intermediates, eg, naphtholsulfonic acids, 4-chloro-1-naphthalenol, and 1-hydroxy-2-naphthoic acid. 1-Naphthalenol is an antioxidant for gasoline, and some of its alkylated derivatives are stabilizers for plastics and rubber (68).

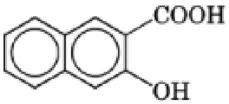
5.2. 2-Naphthalenol

2-Naphthol or β-naphthol or 2-hydroxynaphthalene[135-19-3] melts at 122°C and boils at 295°C, and forms colorless crystals of characteristic, phenolic odor which darken on exposure to air or light. 2-Naphthol [135-19-3] is manufactured by fusion of sodium 2-naphthalenesulfonatewith sodium hydroxide at ca 325°C, acidification of the drowned fusion mass which is quenched in water, isolation and water-washing of the 2-naphthalenol, and vacuum distillation and flaking of the product. A continuous process of this type has been patented (69). The high sulfate content in the primary effluent from 2-naphthol production is greatly reduced in modern production plants by the recovery of sodium sulfate.

Another method of manufacture involves the oxidation of 2-isopropylnaphthalene in the presence of a few percent of 2-isopropylnaphthalene hydroperoxide[6682-22-0] as the initiator, some alkali, and perhaps a transition-metal catalyst, with oxygen or air at ca 90–100°C, to ca 20–40% conversion to the hydroperoxide; the oxidation product is cleaved, using a small amount of ca 50 wt % sulfuric acid as the catalyst at ca 60°C to give 2-naphthalenol and acetone in high yield (70). The yields of both 2-naphthalenol and acetone from the hydroperoxide are 90% or better.

A process variation of the extraction of 2-isopropylnaphthalene hydroperoxide from the crude oxidation product with an alkylene glycol has been patented (71). The 2-naphthalenol plant of American Cyanamid, which was using the hydroperoxidation process and had a 14×10^3 t/yr capacity (72), ceased production in 1982, leaving the United States without a domestic producer of 2-naphthol. The 2-naphthol capacity in the Western world is approximately 50×10^3 t/yr, with ACNA, Italy and Hoechst AG, Germany operating the largest plants. China produces about 7×10^3 t/yr. Other important producing countries are Poland, Romania, the former Czechoslovakia, and India (35, 52).

The principal uses for 2-naphthalenol are in the dyes and pigments industries, eg, as a coupling component for azo dyes, and to make important intermediates, such as 3-hydroxy-2-naphthalenecarboxylic acid (BON) **(28)** and its anilide (naphthol AS), 2-naphtholsulfonic acids, aminonaphtholsulfonic acids, and 1-nitroso-2-naphthol[131-91-9] **(29)**.



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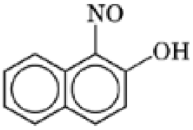

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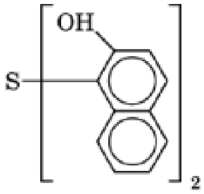
Naphthalenolsulfonic acid formaldehyde condensates are used in tanning agents. Other uses of 2-naphthalenol are in the manufacture of perfuming agents, eg, 2-naphthyl methyl ether[93-04-9] (Yara Yara), R = CH_3 **(30)**, and 2-naphthyl ethyl ether[93-18-5] (nerolin, Bromelia) R = C_2H_5 **(30)**; an antioxidant for polyolefins, ie, thio-1,1-bis(2-naphthol)[17096-15-0] **(31)**; the intestinal antiseptic, 2-naphthyl lactate[93-43-6] (Lactol, Lactonaphthol) **(32)**; a gastrointestinal and genitourinary antiinfective, ie, 2-naphthyl salicylate[613-78-5] (Betol, Salinaphthol), R = OH **(33)**; a semisynthetic penicillin, sodium 6-(2-ethoxy-1naphthamido) penicillanate[985-16-0] (nafcillin sodium, Naptopen, Unipen) **(34)**; an intestinal antiseptic, 2-naphthyl benzoate[93-44-7] (Lintrin, Haertolan) R = H **(33)**; and a topical antifungal agent, tolnaftate[2398-96-1] (*m,N*-dimethylthiocarbanilic acid *O*-naphthyl ester) **(35)**, which is prepared from 2-naphthol, thiophosgene, and *N*-methyl-*m*-toluidine. Naproxen[22204-53-1] **(36)**, an antirheumatic, is also prepared from 2-naphthol by the Friedel-Crafts acylation of 2-methoxynaphthalene and subsequent Willgerodt-Kindler reaction. The S-configuration which is obtained from its racemic mixture with the alkaloid cinchonidine is the effective isomer.



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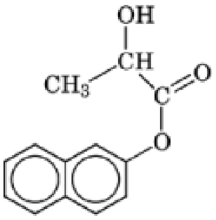

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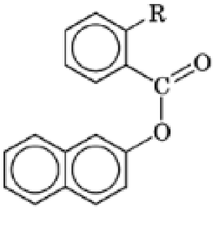

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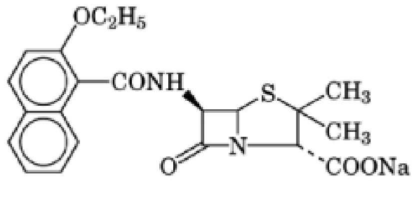

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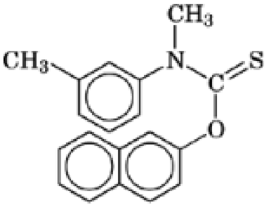

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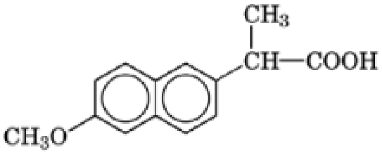

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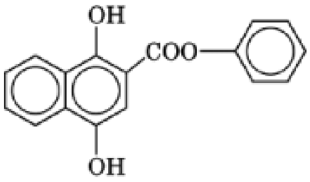
5.3. 1,4-Naphthalenediol

This diol can be prepared by the chemical or catalytic reduction of 1,4-naphthoquinone. Both the diol and quinone are of interest because of their relation to the vitamin K family. Carboxylation of 1,4-naphthalenediol with CO_2–K_2CO_3 followed by neutralization gives 1,4-dihydroxy-2-naphthoic acid (DHNA). DHNA and its aryl esters are useful as intermediates for photochemicals, dyes, and pigments. Phenyl 1,4-dihydroxy-2-naphthoate (PDNA) **(37)** has been prepared by heating DHNA with triphenyl phosphites at 110°C for 10 h (73). The yield is approximately 70%. The principal by-product, which is about 30%, is the ester formed by reaction of PDNA with the starting acid DHNA. An aqueous NaOH solution is added dropwise to an aqueous suspension of this ester at 40–70°C over 1 h and the reaction mixture kept for 2 h to give 86.6% DHNA of 98.7% purity (74), which is then esterified with $(C_6H_5O)_3P$ to obtain PDNA. The esterification process is dramatically improved by adding a small amount of inorganic or organic acid, preferably methanesulfonic acid, benzene sulfonic acid, or naphthalene sulfonic acid; subsequent isolation and crystallization gives a pure product (75).



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5.4. 1,5-Naphthalenediol

1,5-Dihydroxynaphthalene or Azurol is a colorless material which darkens on exposure to air. It is manufactured by the fusion of disodium 1,5-naphthalenedisulfonate with sodium hydroxide at ca 320°C in high yield. 1,5-Naphthalenediol is an important coupling component, giving ortho-azo dyes which form complexes with chromium. The metallized dyes produce fast black shades on wool. 1,5-Naphthalenediol can be aminated with ammonia under pressure to 1,5-naphthalenediamine.

5.5. 1,8-Naphthalenediol

This compound darkens rapidly in air. It can be made by fusion of the sultone of 8-hydroxy-1-naphthalenesulfonic acid with 50 wt % sodium hydroxide at 200–230°C, or by the hydrolytic desulfonation of 1,8-dihydroxy-4-naphthalenesulfonic acid. The diol also reacts with ammonia to give 1,8-naphthalenediamine.

5.6. 2,3-Naphthalenediol

This diol is made by the hydrolytic desulfonation of 2,3-naphthalenediol-6-sulfonic acid at ca 180°C. It is used as a coupler forming azo dyes which are applied in reprographic processes.

5.7. 2,6-Naphthalenediol

This diol is prepared by the alkali fusion of 2-hydroxynaphthalene-6-sulfonic acid (Schaffer acid) at 290–295°C. Schaffer acid is usually produced by sulfonation of 2-naphthol with the addition of sodium sulfate at 85–105°C. This acid is also used as a coupling component in the production of azo dyes such as Acid Black 26. 2,6-Naphthalenediol is used as a component in the manufacture of aromatic polyesters which, as is also true of the corresponding amides, display liquid crystal characteristics (52).

5.8. 2,7-Naphthalenediol

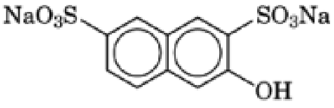
This diol is made by the fusion of sodium 2,7-naphthalenedisulfonate with molten sodium hydroxide at 280–300°C in ca 80% yield. A formaldehyde resin prepared from this diol has excellent erosion resistance, strength, and chemical inertness; it is used as an ablative material in rocket-exhaust environments (76).

6. Hydroxynaphthalenesulfonic Acids

Hydroxynaphthalenesulfonic acids are important as intermediates either for coupling components for azo dyes or azo components, as well as for synthetic tanning agents. Hydroxynaphthalenesulfonic acids can be manufactured either by sulfonation of naphthols or hydroxynaphthalenesulfonic acids, by acid hydrolysis of aminonaphthalenesulfonic acids, by fusion of sodium naphthalenepolysulfonates with sodium hydroxide, or by desulfonation or rearrangement of hydroxynaphthalenesulfonic acids (Table 6).

In the production of sodium 3-hydroxy-2,7-naphthalenedisulfonate[135-59-3] (R-salt) **(38)**, 2-naphthol is stirred with excess 98 wt % sulfuric acid at 60°C, sodium sulfate is added, and the mixture is stirred and heated for 36 h at 105–122°C (77). The charge is diluted with water and salted out with ca 15 wt % sodium chloride at 60°C to give R-salt in 68% yield.

Another example of manufacture of a hydroxynaphthalenesulfonic acid is a caustic fusion process to make 7-hydroxy-2-naphthalenesulfonic acid **(39)** (78). Sodium 2,7-naphthalenedisulfonate, which is made by mixing the 40 wt % disulfonic acid paste with ca 70 wt % caustic, is fused with excess sodium hydroxide in an agitated autoclave at 230–265°C for 10 h. The charge is drowned in water, brought to pH 8 with hydrochloric acid, diluted with water, boiled and treated with carbon, and filtered hot. The product is isolated by filtration after cooling at 30°C. Additional product can be obtained by adding sodium chloride to the filtrate to give a combined yield of 90% of sodium 7-hydroxy-2-naphthalenesulfonate[135-55-7].



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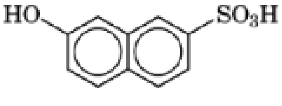

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7. Aminonaphthols and Aminonaphtholsulfonic Acids

The aminonaphthols are of minor use but the aminohydroxynaphthalenesulfonic acids are intermediates for dyes, eg, fiber-reactive azo dyes and plain and metallized azo dyes (Table 7).

The manufacture of 4-hydroxy-6-amino-2-naphthalenesulfonic acid in ca 85% of the theoretical yield has been described (76).

Manufacture of 3-hydroxy-4-amino-1-naphthalenesulfonic acid involves the nitrosation of 2-naphthalenol, bisulfite addition, and reduction of the nitroso to the amino group by sulfur dioxide generated *in situ* (47). 3-Hydroxy-4-amino-1-naphthalenesulfonic acid is obtained in 80% yield.

A number of *N*-acyl-, *N*-alkyl-, and *N*-arylaminonaphthalenolsulfonic acids are used as couplers for azo dyes. Examples of such intermediates are shown in Table 8.

8. Naphthalenecarboxylic Acids

Physical properties for naphthalene mono-, di-, tri-, and tetracarboxylic acids are summarized in Table 9. Most of the naphthalene di- or polycarboxylic acids have been made by simple routes such as the oxidation of the appropriate dior polymethylnaphthalenes, or by complex routes, eg, the Sandmeyer reaction of the selected aminonaphthalenesulfonic acid, to give a cyanonaphthalenesulfonic acid followed by fusion of the latter with an alkali cyanide, with simultaneous or subsequent hydrolysis of the nitrile groups.

Table 6. Manufacture, Production, and Application Data for Selected Hydroxynaphthalenesulfonic Acids

Compound	Trivial name	CAS Registry Number	Manufacturing method[aa,b,c,d,e f]	Intermediate for
4-hydroxy-2-naphthalenesulfonic acid	Armstrong & Wynne's acid; 1,3-oxy-acid	[3771-14-0]	[a,b]	azo dyes, eg, CI Direct Blue 127
4-hydroxy-1-naphthalenesulfonic acid	Nevile-Winther acid; 1,4-oxy-acid	[84-87-7]	[c,d]	azo dyes, eg, CI Acid Red 14; tanning agents
5-hydroxy-1-naphthalenesulfonic acid	L-acid	[117-59-9]	[d,e]	azo dyes and pigments, eg, CI Pigment Red 54, toner; 1,5-naph-thal enediol
8-hydroxy-1-naphthalenesulfonic acid		[117-22-6]	[f]	metallized *o*,*o*′-dihydroxyazo dyes, eg, CI Acid Blue 58
2-hydroxy-1-naphthalenesulfonic acid	oxy-Tobias acid	[567-47-5]	[c]	Tobias acid; J-acid
6-hydroxy-2-naphthalenesulfonic acid	Schaeffer's acid	[93-01-6]	[c]	azo dyes, eg, CI Acid Orange 12; synthetic tanning agents
7-hydroxy-2-naphthalenesulfonic acid	F-acid	[92-40-0]	[e]	azo dyes, eg, CI Direct Blue 128
7-hydroxy-1-naphthalenesulfonic acid	Crocein acid; Baeyer's acid	[132-57-0]	[c]	azo dyes, eg, CI Acid Red 70
4,5-dihydroxy-1-naphthalene-sulfonic acid	dioxy S-acid	[83-65-8]	[e]	azo dyes, eg, CI Direct Blue 26
6,7-dihydroxy-2-naphthalene-sulfonic acid	dioxy R-acid	[92-27-3]	[e]	2,3-dihydroxy-naphthalene
5-hydroxy-2,7-naphthalene-disulfonic acid	RG-acid; violet acid	[578-85-8]	[e]	azo dyes, eg, CI Acid Red 99
8-hydroxy-1,6-naphthalene-disulfonic acid	ϵ-acid; Andresen's acid	[117-43-1]	[f]	azo dyes, eg, CI Direct Blue 98
4-hydroxy-1,6-naphthalene-disulfonic acid	Dahl's acid; D-acid	[6361-37-1]	[a,d]	nitro coloring matter, eg, CI Acid Yellow 1
4-hydroxy-1,5-naphthalene-disulfonic acid	Schoellkopf's acid; CS-acid; δ-acid	[82-75-7]	[f]	azo dyes, eg, CI Acid Blue 169
3-hydroxy-2,7-naphthalene-disulfonic acid	R-acid	[148-75-4]	[c]	azo dyes, eg, CI Acid Red 115, Acid Red 26
7-hydroxy-1,3-naphthalene-disulfonic acid	G-acid	[118-32-1]	[c]	azo dyes, eg, CI Acid Red 73; triphenyl-methane dyes
4,5-dihydroxy-2,7-naphthal-enedisulfonic acid	chromotropic acid	[148-25-4]	[a,e]	azo dyes, eg, CI Acid Violet 3

Table 6. *Continued*

Compound	Trivial name	CAS Registry Number	Manufacturing method[aa,b,c,d,e f]	Intermediate for
8-hydroxy-1,3,6-naphthalene-trisulfonic acid	oxy-Koch's acid	[3316-02-7]	[a]	azo dyes, eg, CI Direct Blue 27; chromotropic acid
7-hydroxy-1,3,6-naphthalene-trisulfonic acid		[6259-66-1]	[c]	azo dyes, eg, CI Acid Red 41

[a] By the hydrolysis of the corresponding aminonaphthalenesulfonic acid.

[b] By the desulfonation of 8-hydroxy-1,6-naphthalenedisulfonic acid.

[c] By the sulfonation of the appropriate (1- or 2-) naphthalenol.

[d] By the Bucherer reaction (with sulfite) of the appropriate aminonaphthalenesulfonic acid.

[e] By the alkali fusion or alkaline hydrolysis under pressure of the appropriate naphthalenedisulfonic or naphthalenetrisulfonic acid or hydroxynaphthalenedisulfonic acid.

[f] By the alkaline hydrolysis of the sultone formed on boiling an aqueous solution of the diazonium salt of 8-amino-1-naphthalenesulfonic acid or its appropriate derivatives.

8.1. 1- and 2-Naphthalenecarboxylic Acids

Naphthalenecarboxylic acids are useful intermediates for dyes and photographic materials. These acids are also used in the preparation of antitumor agents (79) and also in the preparation of cholecystokinin-agonist tetrapeptide (80). The acids are prepared readily by the oxidation of 1- or 2-alkylnaphthalenes with dilute nitric acid, chromic acid, or permanganate. The oxygen or air oxidation of alkylnaphthalenes in an alkanoic acid solvent in the presence of a Ce-, Co-, or Mn-containing catalyst and a Br-containing catalyst gives good results (81–83). The direct carboxylation of naphthalene with CO and oxygen in the presence of a Pd–carboxylate catalyst also has been patented (84). The photo carboxylation of naphthalene in the presence of carbon dioxide and an electron donor has been described. About 67% naphthoic acids were obtained by this method, upon visible light irradiation with phenazine as a sensitizer. Over 90% of the naphthoic acids was 1-naphthoic acid (85).

4-Alkyl-*N,N*-dialkyl-1-naphthalenecarboxamides are useful herbicides (86) and the 2,2-dimethylhydrazide of 1-naphthalenecarboxylic acid has been patented as a plant growth regulator (87). 2-Propynyl-2-naphthalenecarboxylate [53548-27-9] and similar esters are insecticides (88). 1-Naphthaleneacetic acid, the plant growth regulator, has been prepared from naphthalene, concentrated HCl, and paraformaldehyde without isolation of intermediate 1-chloromethylnaphthalene or 1-naphthaleneacetonitrile (89).

1-Naphthaleneacetic acid has also been prepared by the carbonyl-insertion reaction of 1-chloromethylnaphthalene catalyzed by carbonyl cobalt cation (90, 91). Carboxylation of 1-chloromethylnaphthalene in the presence of the catalyst $Pd[P(C_6H_5)_3]_2Cl_2$ under phase-transfer conditions gave 1-naphthaleneacetic acid in 78% yield (92).

Tetrahydrozoline [84-22-0], 2-(1,2,3,4-tetrahydro-1-naphthyl)2-imidazolin, (Tysine, Visine) **(40)**, a sympathomimetic and nasal decongestant, is made by the condensation of 1,2,3,4-tetrahydro-1-naphthoic acid or its methyl ester with 1,2-ethylenediamine.

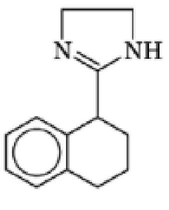
Table 7. Selected Aminonaphthalenols and Aminohydroxynaphthalenesulfonic Acids

Compound	Trivial name	CAS Registry Number	Manufacturing method[abc]	Intermediate for
5-amino-1-naphthalenol	Purpurol	[83-55-6]	[a]	azo dyes, eg, CI Acid Blue 70; sulfur dyes
7-amino-2-naphthalenol	Cyanol	[118-46-7]	[a]	azo dyes, eg, CI Mordant Brown 65
3-hydroxy-4-amino-1-naphthalenesulfonic acid	1,2,4-acid; Boeniger acid	[116-63-2]	[b]	azo dyes, eg, CI Acid Red 186, Mordant Red 7; chrome complex dyes
5-amino-6-hydroxy-2-naphthalene-sulfonic acid	Amino-Schaeffer acid	[5639-34-9]	[c]	photographic developer; rarely used for dyes
4-hydroxy-8-amino-2-naphthalene-sulfonic acid	M-acid	[489-78-1]	[a]	azo dyes, eg, CI Direct Green 42
4-hydroxy-7-amino-2-naphthalene-sulfonic acid	J-acid	[87-02-5]	[a]	azo dyes, eg, CI Direct Blue 71, Direct Red 16; direct dyes using *N*-phenyl J-acid and J-acid imide
4-hydroxy-6-amino-2-naphthalene-sulfonic acid	γ-acid	[90-51-7]	[a]	azo dyes, eg, CI Direct Black 22
4-amino-5-hydroxy-2,7-naphthalene-disulfonic acid	H-acid	[90-20-0]	[a]	azo dyes, eg, CI Direct Black 19, Direct Blue 15
4-amino-5-hydroxy-1,3-naphthalene-disulfonic acid	Chicago acid; SS-acid; 2S-acid	[82-47-3]	[a]	azo dyes, eg, CI Acid Blue 42
4-amino-5-hydroxy-1,7-naphthalene-disulfonic acid	K-acid	[130-23-4]	[a]	azo dyes, eg, Sulfon Acid Blue G, CI 13400
3-amino-5-hydroxy-2,7-naphthalene-disulfonic acid	RR-acid; 2R-acid	[90-40-4]	[a]	azo dyes, eg, CI Direct Brown 31

[a] By the alkali fusion or hydrolysis of the appropriate aminonaphthalenesulfonic acid.

[b] By the nitrosation of 2-naphthalenol and the reaction of the nitroso compound with sodium bisulfite.

[c] By nitrosation/reduction of 6-hydroxy-2-naphthalenesulfonic acid.



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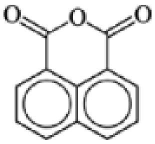

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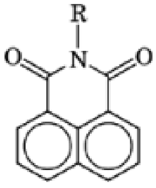

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8.2. 1,8-Naphthalenedicarboxylic Acid

Naphthalic acid readily dehydrates on heating to 1,8-naphthalenedicarboxylic acid anhydride [81-84-5] (naphthalic anhydride) **(41)**. The anhydride and its imide naphthalimide [81-83-4] ($R = H$) **(42)** are intermediates for important dyes, pigments, optical bleaches, and biologically active compounds.

The anhydride can be made by the liquid-phase oxidation of acenaphthene [83-32-9] with chromic acid in aqueous sulfuric acid or acetic acid (93). A postoxidation of the crude oxidation product with hydrogen peroxide or an alkali hypochlorite is advantageous (94). An alternative liquid-phase oxidation process involves the reaction of acenaphthene, molten or in alkanoic acid solvent, with oxygen or acid at ca 70–200°C in the presence of Mn resinate or stearate or Co or Mn salts and a bromide. Addition of an aliphatic anhydride accelerates the oxidation (95).

The anhydride of 1,8-naphthalenedicarboxylic acid is obtained in ca 95–116 wt % yield by the vapor-phase air-oxidation of acenaphthene at ca 330–450°C, using unsupported or supported vanadium oxide catalysts, with or without modifiers (96).

The anhydride of 1,8-naphthalenedicarboxylic acid has fungicidal properties (97). This anhydride has been commercially introduced, under the trade name Protect, as a seed treatment (eg, for corn) to prevent injury to the seed by thiocarbamate herbicides. The effectiveness of the antidote 1,8-naphthalic anhydride has also been successfully studied with several plants and herbicides (98, 99).

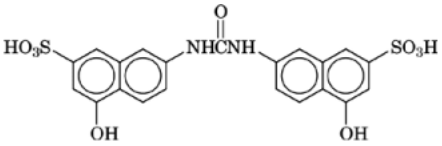
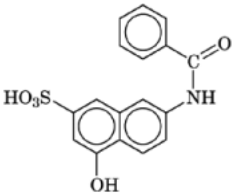
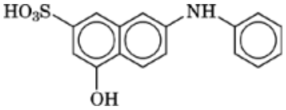
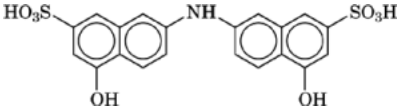
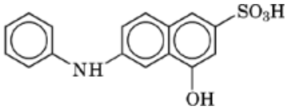
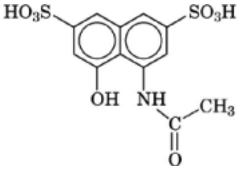
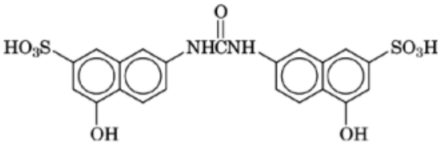
4-Halogenated and 4,5-halogenated derivatives of 1,8-naphthalenedicarboxylic acid anhydride are useful intermediates for dyes, pigments, and fluorescent whiteners for polymers.

Imides of 1,8-naphthalenedicarboxylic acid are used as drugs; an anthelmintic for animals, eg, Naphthalophos; and as rodenticides (100, 101). Other imides are useful fluorescent whiteners for polyesters and acrylonitrile polymers (102). The imide of 1,8-naphthalenedicarboxylic acid gives, by oxidative alkali fusion, the diimide of 3,4,9,10-perylenetetracarboxylic acid, the parent compound of an important class of red dyes and pigments for plastics and coatings with high color fastness. The diimides are useful electrical conductors and semiconductors, eg, in solar-cell systems (103). Some benzimidazole derivatives of 1,8-naphthalenedicarboxylic acid are excellent thickening agents for high temperature greases (104).

8.3. 2,6-Naphthalenedicarboxylic Acid

This dicarboxylic acid, a potential monomer in the production of polyester fibers and plastics with superior properties (105), and of thermotropic liquid crystal polymers (106), is manufactured by the oxidation of 2,6-dialkylnaphthalenes (107, 108).

Table 8. Selected *N*-Substituted Aminohydroxynaphthalenesulfonic Acids

Compound	Structure	Trivial name	CAS Registry Number	Intermediate for
> 7,7′-ureylene-bis-4-hydroxy2-naphthalenesulfonic acid		J-acid urea	[137-47-4]	azo dyes, eg, CI Direct Orange 26
7-benzamido-4-hydroxy2-naphthalenesulfonic acid		*N*-benzoyl J-acid	[132-87-6]	azo dyes, eg, CI Direct Red 81
7-phenylamino-4-hydroxy2-naphthalenesulfonic acid		*N*-phenyl J-acid	[119-40-4]	azo dyes, eg, CI Direct Violet 7
7,7′-imino-bis-4-hydroxy2-naphthalenesulfonic acid		di-J-acid; J-acid imide	[87-03-6]	azo dyes, eg, CI Direct Red 149
6-phenylamino-4-hydroxy2-naphthalenesulfonic acid		*N*-phenyl γ-acid	[119-40-4]	azo dyes, eg, CI Mordant Brown 40
4-acetamido-5-hydroxy-2,7naphthalenedisulfonic acid		*N*-acetyl H-acid	[134-34-9]	azo dyes, eg, CI Acid Violet 7
4-benzamido-5-hydroxy-1,7naphthalenedisulfonic acid		*N*-benzoyl K-acid	[6361-49-5]	azo dyes, eg, CI Acid Red 133

The interest in 2,6-dialkylnaphthalenes such as dimethyl, diethyl, diisopropyl, dihexyl, etc, is shown by the increasing number of patents relevant to their preparation, isomerization, and separation (109–111). No method for selectively preparing 2,6-dialkylnaphthalene has to date been discovered. The efforts that have been made have each failed, not only with conventional Fridel-Crafts catalysts (106, 112, 113), but also with other catalysts such as silica–alumina (114–116) or zeolites in the gas phase (117–120) as well as in the liquid phase (121–123). The Amoco Corp. has patented a process for the selective gas-phase isomerization of the 2,6-dimethylnaphthalene over a lower acidity, supported, molecular sieve-based catalyst composition (124). Amoco has also developed a purification process which uses a monocarboxylic acid anhydride as solvent for adsorption, oxidation, and reduction processes, followed by recrystallization or hydrolysis (125). Purification of dimethyl 2,6-naphthalenedicarboxylate [840-65-3] has been patented by Mitsubishi Gas Chemical Co., Inc. (126). Crude

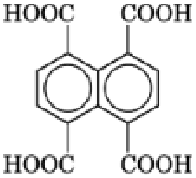
2,6-naphthalenedicarboxylic acid (95% pure), prepared by oxidation of 2,6-diisopropylnaphthalene, was dissolved in an aqueous KOH solution at 70°C and filtered. The filtrate was treated with dimethylacetamide at ordinary temperature and the crystal obtained was dissolved in H_2O, then treated with an aqueous HCl solution to give 87% 2,6-naphthalenedicarboxylic acid of 99.9% purity (127). A Henkel-type process involves either the isomerization under pressure of 1,8-naphthalenedicarboxylic acid at ca 400–500°C in the presence of a CdO catalyst and K_2CO_3 or the carboxylation–isomerization of a naphthalenecarboxylic acid in a similar system. Teijin Ltd. has produced polyester film with good elevated temperature resistance based on 2,6-naphthalenedicarboxylic acid. Teijin's process for the diacid involves the carboxylation–isomerization of the naphthalenecarboxylic acid (128). Cadmium iodide-catalyzed transcarboxylation of naphthalene using potassium salt of benzene carboxylic acid has been investigated at 400°C under pressure of CO_2 (8.1 MPa = 80 atm) to give a high selectivity (90%) of dipotassium 2,6-naphthalenedicarboxylate (129). Also, 2,6-naphthalenedicarboxylic acid can be prepared in high selectivity by the reaction of sodium 2-naphthalenecarboxylate with carbon monoxide, sodium carbonate, and sodium formate at ca 300°C and 2.1–4.8 MPa (300–700 psi) under CO_2 (130). Manufacturing methods for the diacid have been reviewed (131).

8.4. 2,3,6-Naphthalenetricarboxylic Acid

Among the tricarboxylic acids, 2,3,6-naphthalenetricarboxylic acid was found to have an excellent use in materials for functional resins. Thus, Friedel-Crafts acylation of 2,6-dimethyltetralin with acetyl chloride in CH_2Cl_2 in the presence of $AlCl_3$ at 20°C gave 95% 2,6-dimethyl-7-acetyltetralin, which was air-oxidized in acetic acid in the presence of $Co(OOCCH_3)_2{\cdot}4H_2O$, $Mn(OOCCH_3)_2{\cdot}4H_2O$, and KBr at 200°C and 2.9 MPa to give 82% 2,3,6-naphthalenetricarboxylic acid (132).

8.5. 1,4,5,8-Naphthalenetetracarboxylic Acid

Traditionally, the tetracarboxylic acid **(43)** has been manufactured by oxidation of the coal-tar component, pyrene, eg, with chromic acid, or by a chlorination–oleum hydrolysis–oxidation sequence. Also, oxidizing pyrene with aqueous sodium dichromate–sulfuric acid in a sand mill gave 1,6- and 1,8-pyrenequinone in 96% combined yield, further oxidation of which with aqueous KOCl at 80°C gave 51% 1,4,5,8-naphthalene tetracarboxylic acid dianhydride (133). Alternative processes start with acylation of acenaphthene in the 5,6-position followed by an oxidation of naphthalene ring substituents.



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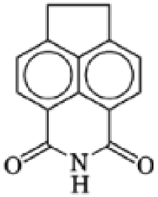

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Table 9. Selected Properties of Naphthalenecarboxylic Acids

Compound	CAS Registry Number	Mp, °C	Other
1-naphthalene-carboxylic acid	[86-55-5]	162	sol ethanol; sparingly sol water; $K_a = 2.04 \times 10^{-4}$ at 25°C; bp at 6.7 kPa[a]
2-naphthalene-carboxylic acid	[93-09-4]	184–185	sol ethanol, ether, chloroform; $K_a = 6.78 \times 10^{-5}$ at 25°C; bp > 300°C
1,2-naphthalenedi-carboxylic acid	[2088-87-1]	175 dec	sol ethanol, ether, acetic acid; mp anhydride 168–169°C
1,3-naphthalenedi-carboxylic acid	[2089-93-2]	267–268	
1,4-naphthalenedi-carboxylic acid	[605-70-9]	309	sol ethanol; insol boiling water
1,5-naphthalenedi-carboxylic acid	[7315-96-0]	315–320 dec	insol common solvents
1,6-naphthalenedi-carboxylic acid	[2089-87-4]	310	sol hot ethanol, aceticacid
1,7-naphthalenedi-carboxylic acid	[2089-91-0]	308	sol common organic solvents
1,8-naphthalenedi-carboxylic acid	[518-05-8]	on heating converts to anhydride (mp 274°C)	sol warm ethanol; bp anhydride at 440 Pa[b] 215°C
2,3-naphthalenedi-carboxylic acid	[2169-87-1]	239–241 dec	sol hot ethanol; mp anhydride 246°C
2,6-naphthalenedi-carboxylic acid	[1141-38-4]	310–313 dec	sol aq alc
2,7-naphthalenedi-carboxylic acid	[2089-89-6]	> 300	sol ethanol
1,2,5-naphthalenetri-carboxylic acid	[36439-99-3]	270–272	sol methanol
1,3,8-naphthalenetri-carboxylic acid	[36440-24-1]		mp 1,8-anhydride 289–290°C
1,4,5-naphthalenetri-carboxylic acid	[28445-09-2]	on heating, forms anhydride (mp undefined)	mp 4,5-anhydride 274°C
1,2,4,5-naphthalene-tetracarboxylic acid	[22246-61-3]	263	mp dianhydride 263°C
1,4,5,8-naphthalene-tetracarboxylic acid	[128-97-2]	on heating, forms anhydride	sol acetone; dianhydride sublimes > 300°C

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert Pa to mm Hg, divide by 133.3.

For example, 5,6-acenaphthenedicarboximide **(44)** can be prepared in 84% yield by the reaction of acenaphthene with excess sodium cyanate in anhydrous HF (78). The intermediate can be oxidized to the tetracarboxylic acid.

The dianhydride of 1,4,5,8-naphthalene tetracarboxylic acid [81-30-1] has been of research interest for the preparation of high temperature polymers, ie, polyimides. The condensation of the dianhydride with *o*-phenylenediamines gives vat dyes and pigments of the benzimidazole type.

8.6. 2,3,6,7-Naphthalenetetracarboxylic Acid

The dianhydride of 2,3,6,7-naphthalenetetracarboxylic acid has also been of interest for the preparation of high temperature polymers, eg, polyimides. It has been prepared by thermal reaction of naphthalene with sodium aromatic carboxylates at 400–500°C in the presence of transcarboxylic catalysts under CO_2 pressure. Thus, autoclaving a mixture of naphthalene, disodium *o*-phthalate, CsI, and CdI_2 at 440°C under 2.45–7.36 MPa (356–1067 psi) CO_2 for 18 h gave 21% naphthalenecarboxylic acids containing 28% 2,3,6,7-naphthalenetetracarboxylic acid (134). 2,3,6,7-Naphthalene carboxylic acid was purified by partial esterification, followed by selective crystallization and separation (135).

Table 10. Selected Properties of Hydroxynaphthalenecarboxylic Acids

Carboxylic acid	CAS Registry Number	Mp, °C	Other
2-hydroxy-1-naphthalene-	[2283-08-1]	157–159	sparing sol H_2O; sol alcohol, benzene
3-hydroxy-1-naphthalene-	[19700-42-6]	248–249	
4-hydroxy-1-naphthalene-	[7474-97-7]	188–188	
5-hydroxy-1-naphthalene-	[2437-16-3]	236	
6-hydroxy-1-naphthalene-	[2437-17-4]	213	
7-hydroxy-1-naphthalene-	[2623-37-2]	256–257	
8-hydroxy-1-naphthalene-	[1769-88-6]	169l	acetone, mp 108°C
1-hydroxy-2-naphthalene-	[86-48-6]	2000.55 wt %	sol in boiling water, alcohol, ether, benzene
3-hydroxy-2-naphthalene-	[92-70-6]	222–2230.1 wt %	sol in water at 25°C, ether, benzene, chloroform
4-hydroxy-2-naphthalene-	[1573-91-7]	225–226	
5-hydroxy-2-naphthalene-	[2437-18-5]	215–216	
6-hydroxy-2-naphthalene-	[16712-64-4]	245–248	
7-hydroxy-2-naphthalene-	[613-17-2]	274–275	
8-hydroxy-2-naphthalene-	[5776-28-3]	229	

9. Hydroxynaphthalenecarboxylic and Aminonaphthalenecarboxylic Acids

Some properties of selected hydroxynaphthalenecarboxylic acids are presented in Table 10.

9.1. 2-Hydroxy-1-Naphthalenecarboxylic Acid

2-Hydroxy-1-naphthoic acid is manufactured by a Kolbe-type process, ie, by reaction of the thoroughly dried potassium or sodium 2-naphthalenolate with CO_2 at ca 115–130°C in an autoclave at ca 300–460 kPa (3.0–4.5 atm) for 10–16 h. It decarboxylates readily, eg, in water starting at ca 50°C.

9.2. 1-Hydroxy-2-Naphthalenecarboxylic Acid

1-Hydroxy-2-naphthoic acid is made similarly to the isomer (2-hydroxy-1-naphthoic acid) by reaction of dry sodium 1-naphthalenolate with CO_2 in an autoclave at ca 125°C. It has been used in making triphenylmethane dyes and metallizable azo dyes. Alkylamides and arylamides of 1-hydroxy-2-naphthalenecarboxylic acid are cyan couplers, ie, components used in indoaniline dye formation in color films (see Color photography).

9.3. 2-Hydroxy-6-Naphthalenecarboxylic Acid

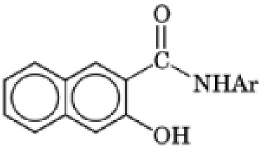
2-Hydroxy-6-naphthoic acid, useful as an intermediate for dyes and a starting material for polyesters, is prepared by stirring the potassium salt of 2-naphthol with the potassium salt of *m*-cresol and high bp distillates of light oil in the presence of 294 kPa (43 psig) CO_2 at 260°C for 1 h (136). A U.S. patent describes the preparation of metal naphthoxide by treating 2-naphthol with cesium or rubidium hydroxide. Metal naphthoxide was dried and then treated with CO_2 ($\sim 140 - 700$ kPa = $20 - 100$ psig) in the presence of cesium or rubidium carbonate and a high boiling solvent to give 36% 2-hydroxy-6-naphthoic acid (137). In another method, sodium salt of 2-naphthol was treated with CO_2 in organophosphine oxide solvents, eg, $(C_4H_9)PO$ at 75–180°C for 3 h to give 2-hydroxy-6-naphthoic acid and 2-hydroxy-3-naphthoic acid in 50% and 40% selectivity (138).

9.4. 3-Hydroxy-2-Naphthalenecarboxylic Acid

3-Hydroxy-2-naphthoic acid or β-oxynaphthoic acid (BON; BONA; Developer 8) **(28)** is the principal commercial product among the hydroxynaphthalenecarboxylic acids. To produce BON, 2-naphthol is first transformed into sodium 2-naphthoate with a 50% sodium hydroxide solution, which is followed by Kolbe-Schmitt carboxylation with CO_2 at temperatures of 235 to 255°C and a pressure of 15 bar; the yield is 90–95% (52, 65). Western European production of 3-hydroxy-2-naphthalene carboxylic acid was over 8×10^3 t in 1985 (52).

By reaction of BON with aniline at 80°C in toluene in the presence of PCl_3, the corresponding amide **(45)** of 3-hydroxy-2-naphthalenecarboxylic acid is produced. The product anilide (Azoic Coupling Component 2) is the base compound of the naphthol AS dyestuffs. Naphthol AS dyestuff components are distinguished from the unsubstituted 2-naphthol derivatives by their increased affinity for the dyed substrate and by higher chemical stability in the atmosphere. Usually the coupling reaction with the diazo salt takes place in the 1-position. Griesheim Red and Indra Red are two earlier used naphthol AS dyestuffs. Also, pigment Red 7 and pigment Red 112 are important naphthol AS pigments. The worldwide production of 2-naphthol AS dyestuffs is about 25×10^3 t/yr (52).

These amides **(45)**, which are of the Naphthol AS type, are important coupling components that are applied to fiber, eg, cotton (qv). They then react with a diazo component on the fiber to produce insoluble azo dyes of high washfastness and lightfastness. A wide range of arylamides of 3-hydroxy-2-naphthalenecarboxylic acids and diazo components is available; azo pigments of similar structure are made from Naphthol AS by coupling a diazo component with a 3-hydroxy-2-naphthalenecarboxamide.



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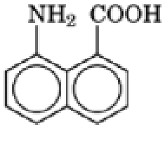

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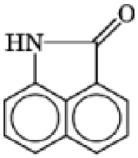


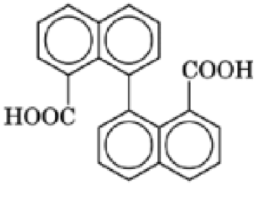
(47)

9.5. 8-Amino-1-Naphthalenecarboxylic Acid

In most methods of 8-amino-1-naphthalenecarboxylic acid **(46)** manufacture, the lactam naphthostyril [130-00-7] **(47)** is obtained. For example, 8-amino-1-naphthalenesulfonic acid is converted to 8-cyano-1-naphthalenesulfonic acid in the Sandmeyer reaction, and the nitrile is treated with concentrated alkali at 185°C to form the lactam. The lactam can be hydrolyzed to the amino acid by treatment with dilute alkali at 100°C

(139). A potentially useful process is the reported treatment of the imide **(42)** of 1,8-naphthalenedicarboxylic acid with sodium hypochlorite to give the lactam **(47)** in 57% yield (140). A procedure has been developed in Germany in which 1,8-naphthalimide is dissolved in an aqueous solution of LiOH and KOH with warming to 40–80°C, the solution is cooled and then chlorine bleaching liquor is added while maintaining the temperature between 10 and 20°C. After the reaction, excess active chlorine is removed reductively, and the pH is adjusted by adding acid to pH 2.0 to give 8-amino-1-naphthalenecarboxylic acid (141). A practical method of manufacture is the preparation of the imide by the reaction of 1-naphthaleneisocyanate with anhydrous aluminum chloride followed by hydrolysis (142).

8-Amino-1-naphthalenecarboxylic acid can be converted, by diazotization and treatment with ammoniacal cuprous oxide, to 1,1′-binaphthalene-8,8′-dicarboxylic acid [29878-91-9] **(48)**. Treatment of **(48)** with concentrated sulfuric acid yields anthranthrone. The dihalogenated anthranthrones are valuable vat dyes.



(48)

The (N-alkylated) lactam of 8-aminonaphthalenecarboxylic acid **(47)** also is a valuable dye intermediate, eg, for cyclomethine-type dyes used for dyeing polyacrylonitrile fibers and other synthetics. 1,8-Naphtholactams are prepared in high yield and purity by the reaction of naphtholactones with RNH_2 ($R = H$, C1–4 alkyl, cycloalkyl, or optionally substituted aryl) in aqueous medium, usually in the presence of bisulfite at 150°C over a period of 15 h (143).

BIBLIOGRAPHY

"Amino Naphthols and Amino Naphtholsulfonic Acids" in *ECT* 1st ed., Vol. 1, pp. 730–737; by J. Werner and A. W. Dawes, General Aniline Works Div., General Aniline & Film Corp.; "Naphthalenesulfonic Acids," "Naphthols and Naphthosulfonic Acids," and "Naphthylamines and Naphthylaminesulfonic Acids" in *ECT* 1st ed., Vol. 9, pp. 232–240, 248–258, and 258–270, by J. Werner, General Aniline Works Div., General Aniline, "Naphthalene Derivatives" in *ECT* 3rd ed., Vol. 15, pp. 719–749, by H. Dressler, Koppers Co., Inc.

Cited Publications

1. F. Radt, ed., *Elsevier's Encyclopedia of Organic Chemistry*, Sec. III, Vols. **12B**, Elsevier, Amsterdam, the Netherlands, 1949–1955.
2. N. Donaldson, *The Chemistry and Technology of Naphthalene Compounds*, E. Arnold Ltd., London, 1958.
3. E. Muller, ed., *Methoden Der Organischen Chemie (Houben-Weyl)*, 4th ed., George Thieme Verlag, Stuttgart, Germany, 1958–present.
4. *Ullmann's Encyklopädie Der Techischen Chemie,* 4th ed., Verlag Chemie, Weinheim/Bergstr., Germany, 1972–present.
5. *Color Index*, 3rd ed., The Society of Dyers & Colorists Publishers, Bradford, U.K., and Research Triangle Park, N.C., 1971; Rev. 3rd ed., 1975.
6. H. A. Lubs, *The Chemistry of Synthetic Dyes and Pigments*, ACS Monograph Series No. 127, Reinhold Publishing Corp., New York, 1955.
7. K. Venkataraman, ed., *The Chemistry of Synthetic Dyes*, **8** vols., Academic Press, Inc., New York, 1952–1978.

8. H. Cerfontain, *Mechanistic Aspects in Aromatic Sulfonation and Desulfonation*, Wiley-Interscience, New York, 1968.
9. N. A. Korneeva, O. M. Prokhorova, and V. V. Kozlov, *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.* **19**, 171 (1976).
10. K. Kaufmann and F. Wolf, *Z. Chem.* **11**, 352 (1971).
11. H. Bretscher, G. Eigemann, and E. Plattner, *Chimia* **32**(5), 180 (1978).
12. R. H. Schreuder, A. Martijn, and C. J. van de Kraats, *Chromatographia* **467**(1), 177–184 (1989).
13. *B.I.O.S. Final Report No. 1152,* Item No. 22, London.
14. Neth. Pat. 138,100 (Feb. 15, 1973), (to Sandoz, AG).
15. Ger. Offen. 2,337,395 (Feb. 15, 1973), (to Farbwerke Hoechst).
16. Rus. Pat. 75 13,792 (Mar. 23, 1970), (to A. Ito and H. Hiyama).
17. Rus. Pat. 53 071,046 (June 24, 1978), (to Sugai Kagaku Kogyo).
18. U.S. Pat. 4,059,609 (Nov. 22, 1977), J. K. Rinehart (to PPG Industries).
19. Y. A. I. Abdel-Aal, E. P. Lampert, M. A. Wolff, and R. M. Roe, *Experientia* **49**, 571 (1993).
20. B. V. Passet, V. A. Kholodnov, and A. V. Matveev, *Zh. Prikl. Khim. 51*, 1606 (1978).
21. U.S. Pat. 4,110,365 (Aug. 29, 1978), S. Bildstein, R. Lademann, S. Peitzsch, and G. Schaeffer (to Hoechst AG).
22. U.S. Pat. 3,655,739 (Nov. 4, 1972), H. Clasen (to Farbwerke Hoechst AG).
23. Ger. Offen. DE 3,937,748 (May 16, 1991), S. Bildstein, J. Heck, D. Schmid, K. Schmiedel, (to Hoechst AG).
24. *FIAT Final Rep. 1016,* 45 (1947).
25. Rus. Pat. 73 38,699 (Nov. 19, 1973), (to Sumitomo Chemical Co.); USSR Pat. 596,565 (Sept. 27, 1977), (to Leningrad Chem. Pharm.).
26. U.S. Pat. 3,546,280 (Dec. 8, 1970), H. Dressler and K. G. Reabe (to Koppers Co.).
27. Jpn. Kokai 78 50,149 (May 8, 1978) H. Fujii, T. Nagashima, and H. Oguri (to Sugai Chemical Industries).
28. Jpn. Kokai Tokkyo Koho JP 63,280,055 (Nov. 17, 1988), A. Yamuchi and co-workers (to Kawasaki Steel Corp.).
29. F. Allison, G. Brunner, and H. E. Feirz-David, *Helv. Chim. Acta* **35**, 2139 (1952).
30. Rus. Pat. 54 467,559 (Apr. 12, 1979), (to Sugai K. K.).
31. Belg. Pat. 866,223 (Oct. 23, 1978), (to Bayer AG).
32. *Chem. Eng. News* **54**, 11 (June 23, 1975); *Chem. Age*, 3 (Feb. 13, 1976).
33. USSR SU 1,742,254 (June 23, 1992), S. T. Babaev and co-workers (to Scientific Research Institute of Concrete and Reinforced Concrete).
34. Eur. Pat. Appl. EP 488,217 (June 3, 1992), H. Fuzimoto, T. Ishikawa, and K. Yoshida.
35. *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1994.
36. USSR Pat. 267,889 (July 24, 1970), (to Phys. Org. Chem. Inst. Acad. Sci. Beloruss, SSR); USSR Pat 443,885 (June 5, 1975), T. I. Vasilenok, and co-workers.
37. *B.I.O.S. Final Report 1143,* London.
38. L. Eberson, M. P. Hartshorn, and Radner, *Finn. J. Chem. Sec., Perkin Trans.* **2**(10) 1793–1798 (1992).
39. *Chem. Eng. News* **55**, 7 (Jan. 3, 1977).
40. U.S. Pat. 4,053,526 (Apr. 19, 1975), (to Bayer AG); Rus. Pat. 54,016,460 (Feb. 2, 1979), (Nippon Synthetic Chemicals Industries).
41. Brit. Pat. 1142628 690212 (1969), S. Suzuki, M. Kurata, A. Akiyoshi, S. Aoshima, D. Hirohiko, and N. Matsuoka.
42. Brit. Pat. 1173890 691210 (1969), A. A. Artem'ev, Y. A. Strepikheev, Y. A. Shmidt, and B. M. Babkin.
43. V. Vijayakumaran, S. Muralidharan, C. Ravichandran, S. Chellammal, and P. N. Anantharan, *Bull. Electrochem.* **6**(5), 522–523 (1990).
44. F. Mahdavi, T. C. Bruton, and Y. Li, *J. Org. Chem.* **58**, 744–746 (1993).
45. USSR SU 292,474 (Apr. 23, 1984), S. V. Dobrovolskii and co-workers.
46. X. Yang, *Huaxue Shijie* **25**(1), 10–12, (1984).
47. Rus. Pat. 43008808 680408 (1968), S. Kano and co-workers (to Japan Soda Co., Ltd.).
48. Chn. Pat. 10-59905 A 920401 (1992), Y. Jingguo (to Donghe Chemical Co., Ltd.).
49. Hung. Pat. 18824 800927 , (1980), I. Besan and co-workers (to Nehezvegyipari Kutato Intezet).
50. Ger. Offen. 2,523,351 (Dec. 9, 1976), (to Bayer AG); Jpn. Pat 50 0970,954 (July 26, 1975), (to Mitsui Toastu Chemical Co.).
51. Ger. Offen. DE 4,025,131; (Feb. 1992), (to Bayer AG).
52. H.-G. Franck and J. W. Stadelhofer, *Industrial Aromatic Chemistry*, 1988, Chapt. 9.
53. *B.I.O.S. Document FD 4637/47,* frames 58–60, London.

54. Czech. CS 256,840 (Feb. 1, 1989), J. Kroupa and co-workers.
55. PB Report 74197, Washington, D.C.
56. Jpn. Kokai Tokkyo Koho JP 03,106,843 (May 7, 1991), S. Yamauchi and Y. Isuda (to Osaka Gas Co., Ltd.).
57. G. A. Olah and co-workers, *J. Org. Chem.* **56**, 6148–6151 (1991).
58. V. I. Trofimov, Y. Levkov, and A. M. Yakubson, *Sov. Chem. Ind.* **3**, 168 (1973).
59. *Chem. Eng. News* **53**, 25 (July 28, 1975).
60. U.S. Pat. 5066819A 911119, (1991), G. H. Kulkarni, R. H. Naik, and S. Rajappa (to Council of Scientific and Industrial Research (India)).
61. U.S. Pat. 3,480,671 (Nov. 25, 1969), H. Files and co-workers (to Stauffer).
62. S. Huang and P. Liu, *Huaxue Shiji* **14**(5), 313, (1992).
63. P. K. Jain and S. K. Srivastava, *J. Indian Chem. Soc.* **69**(7), 402–403 (1992).
64. M. Purohit and S. K. Srivastava, *Proc. Nat. Acad. Sci., India, Sect. A.* **61**(4), 461–464 (1991).
65. K. Moersdorf and G. Wolf, *Dtsch. Med. J.* **17**(10), 303–306, (1967).
66. U.S. Pats. 3,337,628 (Aug. 22, 1967) and 3,520,919 (July 21, 1970), S. Crowther (to I. C. I.).
67. S. P. Kamat, S. K. Paknikar, *Indian J. Chem., Sect. B*, **27B**(8), 773–774, (1988).
68. S. P. Starkov and Y. I. Mostyaev, *Sov. Chem. Ind.* **5**, 302 (1973).
69. USSR Pat. 340,270 (Jan. 31, 1973), (to Novosibirsk Org. Chem. Inst. Siberian Academy of Sciences USSR).
70. Brit. Pat. 654,035 (May 30, 1951), W. Webster and D. C. Quin (to the Distillers Co. Ltd.); U.S. Pat. 3,804,723 (Apr. 16, 1974), J. P. Dundon, H. R. Kemme, and E. J. Scharf (to American Cyanamid Co.); U.S. Pat. 3,848,001 (Nov. 12, 1974), J. P. Dunden (to American Cyanamid Co.); U.S. Pat. 3,939,211 (Feb. 17, 1976), R. H. Spector and R. K. Madison (to American Cyanamid Co.); U.S. Pat. 4,021,495 (May 3, 1977), H. Hosaka, K. Tamaka, and Y. Ueda (to Sumitomo Chemical Co.); U.S. Pat. 4,049,720 (Sept. 20, 1977), H. Hosaka, K. Tamimoto, and H. Yamachika (to Sumitomo Chemical Co.); Ger. Offen. 2,207,915 (Aug. 23, 1973), M. Elstner, H. Hoever, and M. Fremery (to Union Rheinishe Braunishe Braunkohlen Kraftsoff AG): Ger. Offen. 2,517,591 (Oct. 23, 1975), M. Takahashi, T. Yamanchi, and T. Imura (to Kureha Chemical Industries); USSR Pat. 498,292 (Jan. 5, 1976), M. I. Ferberov, B. N. Bychkov, G. N. Shustovskaya, and G. D. Mantyukov (to Yaroslavl Polytechnic Institute); USSR Pat. 593,729 (Mar. 9, 1976); M. I. Ferberov, B. N. Bychkov, G. N. Shustovskaya, and G. D. Mantyukov (to Yaroslavl Polytechnic Institute).
71. Jpn. Kokai 75 0076,054 (June 21, 1975), K. Kobayaschi, I. Dogane, and Y. Nagao (to Sumitomo Chemical Industries).
72. *J. Commerce*, 325 (June 26, 1972).
73. Jpn. Kokai Tokkyo Koho JP 01 45,341 (Feb. 17, 1989), T. Sonoda and co-workers (to Nippon Shokubai Kagaku Kogyo Co., Ltd.).
74. Jpn. Kokai Tokkyo Koho JP 01 45,342 (Feb. 17, 1989), T. Sonoda and co-workers (to Nippon Shokubai Kagaku Kogyo Co., Ltd.).
75. Eur. Pat. Appl. EP 405,928 (Jan. 2,1991) Y. Maegawa and Y. Nishida (to Sumitomo Chemical Co., Ltd., and Deiei Chemical Co., Ltd.).
76. U.S. Pat. 3,391,117 (July 2, 1968), N. Bilow and L. J. Miller (to U.S. Department of the Air Force); *Chem. Week,* 84 (Aug. 21, 1965).
77. *FIAT Final Report No. 1016,* 22–23.
78. Ger. Offen. 2,304,873 (Aug. 8, 1974), K. Eiglmeier and H. Luebbers (to Farbwerke Hoechst AG).
79. Eur. Pat. Appl. EP 390,181 (Oct. 3, 1990), T. Kishi and co-workers (to Kyowa Hakko Kogyo Co. Ltd.).
80. PCT Int. Appl. WO 90 06, 937 (June 28, 1990), (to . 21, 1988), K. Shiosaki and co-workers (to Abbott Laboratories).
81. Fr. Pat. 1,543,144 (Oct. 18, 1868), G. J. Rolman (to Ashland Oil); USSR Pat. 225,249 (Oct. 29, 1970), N. D. Rusyanova and N. S. Mulyaeva (to Eastern Scientific Research Institute of Coal Chemicals); Jpn. Pats. 73 43,891 and 73 43,893 (Dec. 21, 1973), G. Yamashita and K. Yamamoto (to Teijin Ltd.).
82. Jpn. Kokai Tokkyo Koho JP 02,240,046 (Sept. 25, 1990), T. Sato and co-workers (to Sumikin Coke Co., Ltd.).
83. Jpn. Kokai Tokkyo Koho JP 02,250,850 (Oct. 8, 1990), Y. Doko and Y. Teruaki (to Sumikin Coke Co., Ltd.).
84. U.S. Pat. 3,920,734 (Nov. 18, 1975), Y. Ichikawa and Y. Yamaji (to Teijin Ltd.).
85. H. Tagaya and co-workers, *Bull. Chem. Soc. Jpn.* **63**(11), 3233–3237 (1990).
86. Ger. Offen. 2,028,555 (Dec. 17, 1970), E. Arsuro and co-workers (to Montecatini Edison SpA).
87. U.S. Pat. 3,855,289 (Dec. 17, 1974), G. H. Alt (to Monsanto Co.).
88. Ger. Offen. 2,824,988 (Dec. 21, 1978), M. Suchy (to F. Hoffmann-La Roche and Co.).
89. Hung. Pat. 50095 A2 891228 (1989), L. Balogh and co-workers (to Alkaloida Vegyeszeti Gyar, Hung. Teljes).

90. Jpn. Kokai Tokkyo Koho, JP 62158243 A2 870714 , (1987), T. Ikeda and co-workers (to Denki Kogaku Kogyo K.K.).
91. X. Shen and co-workers, *Ziran Kexueban* **1**, 6–13 (1981).
92. X. Huang and co-workers, *Ziran Kexueban* **17**(4), 499–500 (1990).
93. USSR Pat. 517,579 (Sept. 6, 1976), L. A. Kozorez and co-workers (to Voroshilovgrad Mechanical Institute).
94. Brit. Pat. 1,224,418 (Mar. 10, 1971), (to Mitsubishi Chem. Ind.); U.S. Pat. 3,646,069 (Feb. 29, 1972), H. Okada and co-workers (to Sandoz Ltd.); Jpn. Kokai 76 11,749 (Jan. 30, 1976), Y. Wakisada and M. Sumitami (to Nippon Kayaku Co.).
95. Ger. Pat. 1,262,268 (Mar. 7, 1968); A. Marx and co-workers (to Rutgerswerke AG); USSR Pat. 291,910 (Jan. 6, 1971), V. L. Plakin and co-workers; Ger. Offen. 2,520,094 (Nov. 20, 1975), H. Okushima, I. Nitta, and R. Furuya (to Mitsui Petrochem, K.K.); Rus. Pat. 53 141,253 (Dec. 12, 1978), (to Nippon Kayaku K.K.).
96. Belg. Pat. 525,660 (June 8, 1956), (to Rutgerswerke AG); Rus. Pat. 71 13,737 (Apr. 13, 1971), Y. Shimada, H. Yoshizumi, and Namikiri (to Japan Catalytic Chemical Industrial Co.); U.S. Pat. 3,708,504 (Jan. 2, 1973), O. Kratzar, H. Suter, and F. Wirth (to Badische Anilin and Soda Fabrik AG); Jpn. Kokai 75 39,292 (Apr. 11, 1975), Y. Nanba and co-workers (to Japan Catalytic Chemical Industrial Co.); USSR Pat. 535,306 (Dec. 20, 1976), D. Kh. Sembaev and co-workers (to AS Kazakistan Chemical Sciences).
97. U.S. Pat. 3,860,720 (Jan. 14, 1975), M. F. Covey (to Gulf Research & Development Co.).
98. M. Jain and co-workers, *Indian J. Plant Physiol.* **32**(2), 185–187 (1989).
99. D. I. Chkanikov and co-workers, *Fiziol Rast. (Moscow)* **38**(2), 290–296 (1991).
100. U.S. Pats. 3,940,397 and 3,940,398 (Feb. 24, 1976); 3,947,452 (Mar. 30, 1976); 3,959,286 (May 25, 1976); 3,996,363 (Dec. 7, 1976); 4,007,191 (Feb. 8, 1977); 4,051,246 (Sept. 27, 1977); 4,062,953 (Dec. 13, 1977); 4,070,465 (Jan. 24, 1977), P. C. Wade and B. R. Vogt (to E. R. Squibb & Sons, Inc.).
101. Can. Pat. 1,030,147 (Apr. 25, 1978), R. Martinez and co-workers (to Laboratories Made SA).
102. Ger. Offen. 2,507,459 (Sept. 2, 1976), (to Badische Aniline and Soda Fabrik AG).
103. Ger. Offen. 2,636,421 (Feb. 16, 1978), (to Badische Aniline and Soda Fabrik AG).
104. U.S. Pat. 4,040,968 (Aug. 9, 1977), H. A. Harris (to Shell Oil Co.).
105. Jpn. Kokai Tokkyo Koyo 75 0076 054 (1975), K. Kobayaschi and co-workers.
106. U.S. Pat. 4288646, (1979), G. A. Olah.
107. Jpn. Kokai Tokkyo Koho 57203032 (1981), (to Toray Industries Inc.).
108. Jpn. Kokai Tokkyo Koho JP 04 99,749 (Mar. 31, 1992) Y. Koko and R. Minami (to Sumikin Kako K.K).
109. PCT Int. Appl. Wo 90 03961 , (1990), J. D. Fellman and co-workers.
110. Jpn. Kokai Tokkyo Koyo 02 264 733 (1990) (to 0) K. Tate, Y. Sasaki, and T. Sasaki.
111. Jpn. Kokai Tokkyo Koyo 03 167 139 , (1991), T. Fujita and co-workers.
112. F. Radt, in F. Radt, *Elsevier's Encyclopedia of Organic Chemistry*, Vol. **12B**, Elsevier Publishing Co., New York, 1948, 132–161.
113. G. A. Olah and J. A. Olah, *J. Amer. Chem. Soc.* **98**, 1839 (1976).
114. W. M. Kutz and B. B. Corson, *J. Amer. Chem. Soc.* **67**, 1312 (1945).
115. Rus. Pat. 74 48949 (1974), (to Teijin Co. Ltd.).
116. A. V. Topchiev and co-workers, *Dokl. Akad. Nauk SSSR* **139**, 124 (1961).
117. B. Chiche and co-workers, *J. Org. Chem.* **51**, 2128 (1986).
118. W. N. Kaeding and co-workers, *J. Catal.* **67**, 159 (1981).
119. D. Fraenkel and co-workers, *J. Catal.* **101**, 273 (1986).
120. Ger. Offen. DE 3334084 (1985), K. Eichler and E. I. Leupold.
121. P. Moreau and co-workers, *J. Catal*, in press.
122. A. Katayama and co-workers, *J. Chem. Soc., Chem. Commun.*, 39 (1991)
123. P. Moreau, *J. Org. Chem.* **57**, 5040 (1992).
124. U.S. Pat. 4,783,569 (Nov. 8, 1988), G. P. Hussmann and P. E. McMahon (to Amoco Corp.).
125. U.S. Pat. 5,097,066 (Mar. 17, 1992) J. K. Holzhauer and G. E. Kuhlmann (to Amoco Corp.).
126. Jpn. Kokai Tokkyo Koho JP 03,258,753 (Nov. 19, 1991), T. Tanaka and H. Fujita (to MGC Co. Inc.).
127. Jpn. Kokai Tokkyo Koho Jp 02,243,652 (Sept. 27, 1990), M. Morita and co-workers (to Nippon Steel Chemical Co., Ltd.).
128. *Chem. Week* **112**, 43 (Apr. 25, 1973).
129. K. Kudo, S. Mori, and N. Sugita, *Bull. Inst. Chem. Res., Kyoto Univ.* **70**(3), 284 (1992).

130. U.S. Pat. 3,718,690 (Feb. 278, 1973), R. D. Bushick, O. L. Norman, and H. J. Spinnelli.
131. I. I. Kiiko, *Khim. Prom.* **1**, 13 (1975).
132. Jpn. Kokai Tokkyo Koho JP 01,228,939 (Sept. 12, 1989), Y. Sato and Y. Tanaka (to Sumikin Kako Co., Ltd.).
133. V. A. Shigalevskii and co-workers, *Zh. Org. Khim.* **21**(7), 1506–1513 (1985).
134. Jpn. Kokai Tokkyo Koho JP 04,224,544 (Aug. 13, 1992), Y. Tachibana and co-workers (to Nippon Kokan K.K.).
135. Jpn. Kokai Tokkyo Koho Jp 04 89,453 (Mar. 23, 1992), Y. Tachibana and co-workers (to Nippon Kokan K.K.).
136. Jpn. Kokai Tokkyo Koho JP 03,223,230 (Oct. 2, 1991), T. Suzuki and co-workers (to Kawasaki Steel Corp.).
137. U.S. Pat. 5,075,496 (Dec. 24, 1991), J. Pugach and D. T. Derussy (to Aristech Chemical Corp.).
138. Jpn. Kokai Tokkyo Koho JP 03,200,741 (Sept. 2, 1991), T. Nakanishi and T. Miura.
139. *Product Bulletin IC-4,* American Cyanamid Co., July 1978.
140. *B.I.O.S. Final Rep. No. 1152,* London, 118–123.
141. Ger. Pat. 3535482 AI 870409 (1987), O. Arndt and T. Papenfuhs (to Hoechst AG).
142. T. Maki, S. Hashimoto, and K. Kamada, *J. Chem. Soc. Jpn. Ind. Chem. Sect.* **55**, 4835 (1952).
143. Eur. Pat. 84853 AI 830803 (1983), R. Begrich (to Ciba-Geigy AG).

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