Kirk-Othmer Encyclopedia of Chemical Technology.

Amines, Aromatic

AMINES, AROMATIC, PHENYLENEDIAMINES

Phenylenediamines are aromatic amines with two amino groups attached to benzene. They are called benzenediamines by *Chemical Abstracts*. There are three phenylenediamines; ortho, meta, and para; or 1,2-; 1,3-; and 1,4-benzenediamines, respectively. Since they are difunctional, they are easily converted to polymers. The *m*-phenylenediamines are the least expensive isomers and are used in the largest volumes for the manufacture of polyurethanes (see Urethane polymers). *p*-Phenylenediamine is used for the manufacture of polyamides with exceptional tensile strength (see High performance fibers; Polyamides; and Polyimides). The use of *o*-phenylenediamines for polymer formation is limited, but polybenzimidazoles and polyquinoxalines have been made (see Heat-resistant polymers). However, it is the unique chemistry of the *p*-phenylenediamine derivatives that makes them useful in the photographic and dye industries, and widely used as antioxidants (qv) and antiozonants (qv) for rubbers and plastics (see Azine dyes; Azo dyes; Color photography; Cosmetics; Hair preparations; and Sulfur dyes).

1. Physical Properties

The three phenylenediamines are all white solids when pure, but darken after standing in air. They are all very soluble in hot water, for example, about 700 g of *o*- or *p*-phenylenediamine are soluble in 100 mL of water at 100°C whereas at room temperature only 4 g dissolve. The physical properties of the phenylenediamines and some of their more important derivatives are given in Table 1. Certain imines of *p*-phenylenediamine are liquid crystals (1). For example, N,N′-bis[*p*-(octadecyloxy)benzylidene]-*p*-phenylenediamine [24679-0508] has a mp of 129, 147, and 183°C (see Liquid crystalline materials).

2. Chemical Properties

The phenylenediamines are aromatic amines which undergo typical amine reactions, such as *N*-acylation and *N*-alkylation. However, unlike most aromatic amines, they cannot easily be alkylated on the aromatic ring using an olefin and an acid catalyst since protonation of the second amino group deactivates the ring. Consequently, most of the chemistry of the phenylenediamines involves reactions on the nitrogen. Commercially the largest volume usage of phenylenediamines is in the manufacture of diisocyanates; large volumes of *N,N′*-alkyl/aryl-*p*-phenylenediamines are also manufactured.

o-Phenylenediamines favor the formation of five- and six-membered rings and undergo many reactions which involve cyclization to give heterocyclic compounds. Anhydrides, acids, amides, and esters give benzimidazoles (2); cyanogen chloride gives the 2-aminobenzothiazole (3); 1,2-dicarbonyl compounds (4) and propargyl alcohols (5) give quinoxalines; methyl ketones give 1,5-benzodiazepines (6); *o*-chlorobenzoic acids (7) and chromones and flavones give benzodiazepinediones (8); β-ketoesters give benzodiazepinones (9); nitrous acid

Table 1. Physical Properties of Phenylenediamines

Phenylenediamine	Molecular formula	CAS Registry Number	Appearance	MP, °C	BP[a], °C	Synthetic route	Price $/kg
orthophenylenediamine[b]	$C_6H_8N_2$	[95-54-5]	white solid	102	256–258 (dec)	ammonol, reduction of *o*-chloronitrobenzene	7.16
metaphenylenediamine[b]	$C_6H_8N_2$	[108-45-2]	white solid	63	287	catalytic reduction of *m*-dinitrobenzene	4.56
paraphenylenediamine[b]	$C_6H_8N_2$	[106-50-3]	white solid	140	267	ammonol, reduction of *p*-chloronitrobenzene	8.82
toluene-2,4-diamine	$C_7H_{10}N_2$	[95-80-7]		99	280	reduction of 2,4-dinitro-toluene	
toluene-2,6-diamine	$C_7H_{10}N_2$	[823-40-5]		105		reduction of 2,6-dinitro-toluene	2.82[c]
2,3,5,6-tetramethyl-*p*-phenylenediamine	$C_{10}H_{16}N_2$	[3102-87-2]	tan colored	151–152		nitration, reduction of durene	
N,N-dimethyl-*p*-phenylenediamine	$C_8H_{12}N_2$	[99-98-9]		41	262	nitrosation, reduction of *N,N*-dimethylaniline	
N,N-diethyl-*p*-phenylenediamine	$C_{10}H_{16}N_2$	[93-05-0]	pale yellow oil		260–262	reduction of *p*-nitro-*N,N*-diethylaniline	
N,N′-bis(1-methylpropyl)-*p*-phenylenediamine	$C_{14}H_{24}N_2$	[101-96-2]	pale yellow oil		98 (26.6 Pa[d])	reductive alkylation of *p*-phenylenediamine	
N,N′-bis(1-methylheptyl)-*p*-phenylenediamine	$C_{22}H_{40}N_2$	[103-96-8]	low melting white solid		190 (40 Pa[d])	reductive alkylation of *p*-phenylenediamine	6.81
N,N′-bis(1-methylpropyl)-*N,N′*-dimethyl-*p*-phenylenediamine	$C_{16}H_{28}N_2$	[87-98-9]	oil		115 (20 Pa[d])	Leuckart-Wallach reaction	
N-phenyl-*p*-phenylenediamine	$C_{12}H_{12}N_2$	[101-54-2]		75	354	nitrosation, reduction of diphenylamine	
N,N′-diphenyl-*p*-phenylenediamine	$C_{18}H_{16}N_2$	[74-31-7]	white solid	146		from hydroquinone and aniline, acid cat	10.38
N,N′-di-2-naphthalenyl-*p*-phenylenediamine	$C_{26}H_{20}N_2$	[93-46-9]		236		from 2-naphthol and *p*-phenylenediamine, heat	13.78
N-1-methylethyl-*N′*-phenyl-*p*-phenylenediamine	$C_{15}H_{18}N_2$	[101-72-4]		78		reductive alkylation of *N*-phenyl-*p*-phenylene-diamine	7.61
N-(1,3-dimethylbutyl)-*N′*-phenyl-*p*-phenylenediamine	$C_{18}H_{24}N_2$	[793-24-8]		48–50		reductive alkylation of *p*-aminodiphenylamine with methyl isobutyl ketone	7.14
N-cyclohexyl-*N′*-phenyl-*p*-phenylenediamine	$C_{18}H_{22}N_2$	[101-87-1]				reductive alkylation of *p*-aminodiphenylamine with cyclohexanone	7.54

[a] At $101.3\ \text{kPa} = 1\ \text{atm}$ unless otherwise noted.

[b] The K_bs of *o*-, *m*-, and *p*-phenylenediamine are 3.2×10^{-10}, 7.6×10^{-10}, and 1.1×10^{-8}, respectively.

[c] Price of the mixed diisocyanate.

[d] To convert Pa to mm Hg, multiply by 0.0075.

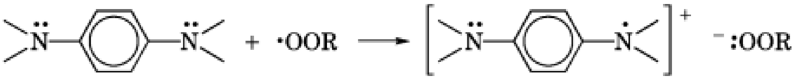
gives triazoles; and phosphorus and boron compounds (10) give five-membered ring heterocyclic compounds. Large ring annulenes can also be prepared from certain α,β-unsaturated aldehydes (11).

The *p*-phenylenediamines are special and are used in many applications where the other isomers are ineffective. They are unique because they are more readily oxidized than the meta or ortho isomers, as seen by

Table 2. Ionization Potentials of Phenylenediamines

Compound	CAS Registry Number	Ionization potential, eV
N,N,N′,N′-tetramethyl-*p*-phenylenediamine	[100-22-1]	5.97
N,N-diethyl-*p*-phenylenediamine	[93-05-0]	6.04
p-phenylenediamine	[106-50-3]	6.52
m-phenylenediamine	[108-45-2]	7.26
o-phenylenediamine	[95-54-5]	7.29
aniline	[62-53-3]	7.70

the ionization potentials listed in Table 2. The enhanced reactivity of *p*-phenylenediamine is due to the high degree of resonance stabilization of its radical cation.

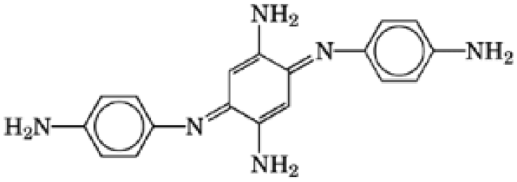


Most oxy or halo free radicals readily oxidize *p*-phenylenediamines to radical cations called Wurster salts (12), which are stable in water-ethanol solutions at pH 3. On the other hand, carbon and sulfur radicals generally do not produce Wurster salts. The intense color of Wurster salts can be used as a quick spot test for variously substituted *p*-phenylenediamines when oxidized with bromine in carbon tetrachloride solution. For example, *N,N′*-dialkyl substitution gives red, *N,N,N′,N′* gives blue, and *N*-alkyl-*N′*-aryl gives light blue or green.

Because of their ease of oxidation, *p*-phenylenediamines are used as antioxidants, antiozonants, dye intermediates, and reducing agents in color photography. This is clearly seen with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, which has no labile hydrogen atom, yet still functions as an antioxidant by reducing peroxy radicals into anions. The facile one-electron oxidation of *N,N*-dialkyl-*p*-phenylenediamine makes it an important developing agent of light-sensitized silver salts in color photography (13). Similarly, oxidation of a mixture of 2,5-toluenediamine [95-70-5], aniline, and *o*-toluidine gives a red azine dye, Safranine T: oxazines and thiazines are made in an analogous way (14). Azomethine dyes are obtained when a *p*-phenylenediamine is oxidized in the presence of compounds containing active hydrogens (15).

Among aromatic amines, only *p*-phenylenediamines exhibit antiozonant activity because they react faster than other aromatic amines with ozone (see Antiozonants). Undoubtedly, this is due to their low ionization potential and their ability to react free-radically with ozone. Besides scavenging the ozone, *p*-phenylenediamines react with ozone to form high molecular weight products which act as physical barriers to ozone and retard further attack. The chemistry of this process involves reactions at three sites: (*1*) The side chain is oxidized to yield amides, nitro, and nitroso compounds, (*2*) the phenylenediamine ring is oxidized to quinonediimines (and their oxides) which add free amine to produce high molecular weight Bandrowski bases, (*3*) dimerization through the nitrogens give hydrazines (16). All of the above products can form from the first reaction product of ozone with the *p*-phenylenediamine, the Wurster salt.

An important mode of oxidation for *p*-phenylenediamines is the formation of *p*-benzoquinonediimines, easily obtained by oxidation with silver oxide in ether solution (17). Diimines undergo 1,4 additions with amines to generate tri- and tetraamines which readily oxidize in air to highly conjugated, colored products. An example of this is the formation of Bandrowski's base [20048-27-5] when *p*-phenylenediamine is oxidized with potassium ferricyanide (18).



Bandrowski's base

Most diimines are unstable and polymerize with great ease. They also readily hydrolyze to amines and quinones. Thus *p*-phenylenediamine can be oxidized directly to *p*-benzoquinone with manganese dioxide in aqueous sulfuric acid. Alkyl substitution increases stability only slightly whereas the *N*-aryl or *N,N*′-diaryl derivatives are stable. *N,N*′-Diphenyl-*p*-benzoquinonediimine [6246-98-6] is an orange solid, mp 187°C, prepared by heating *N,N*′-dinitroso-*N,N*′-diphenyl-*p*-phenylenediamine [2716-09-8] at about 100°C. *N,N*′-Dibenzene-sulfonyl-*p*-benzoquinonediimine [1050-82-4], mp 179°C, readily undergoes Diels-Alder addition reactions with dienes, whereas the *N*-aryl diimines react sluggishly (19). *o*-Phenylenediamine is also oxidized to *o*-benzoquinonediimine [4377-73-5] by silver oxide in ether.

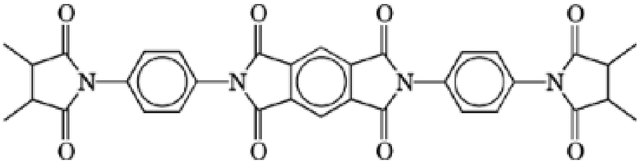
Both the *m*- and *p*-phenylenediamines are used to manufacture sulfur dyes, either by refluxing in aqueous sodium polysulfide, or heating with elementary sulfur at 330°C to give the leuco form of the dye. These dyes are polymeric, high molecular weight compounds, and soluble in base. The color is developed by oxidation on the fabric. 2,4-Toluenediamine and sulfur give Sulfur Orange 1 (14).

p-Phenylenediamines can be diazotized and tetrazotized (20), giving intermediates for various azo dyes (qv). Their diazonium salts are commercially manufactured and used in photography.

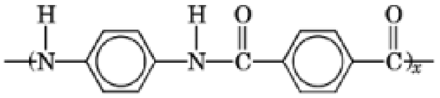
3. Polymerization

Until the mid-1960s, phenylenediamines were used primarily for oxidative purposes; the para isomer was of major importance. Since then, the use of phenylenediamines to manufacture polymers has far exceeded their use for oxidative purposes. The *m*-phenylenediamines, (2,4 and 2,6)-toluenediamine, are widely used for the manufacture of polyurethanes. Phenylenediamines are difunctional and react with other difunctional compounds, such as dianhydrides, diacyl chlorides, dicarboxylic acids, and disulfonyl chlorides to give polyamides. Phenylenediamines also give polymers with epoxides, diols, diacetals, diisocyanates, diesters, etc. These aromatic polymers are being investigated for high temperature applications (see Heat-resistant polymers), and for use as electric conductors (21) (see Electrically conductive polymers).

p-Phenylenediamine is used to make heat-resistant polyimides by reaction with pyromellitic anhydride (see Polyimides).

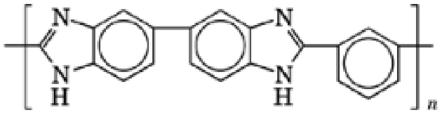


Both *m*- and *p*-phenylenediamine react with benzenedicarbonyl dichlorides to give linear, fully aromatic polyamides (see High performance fibers).



Polymers from the meta isomer are useful for their heat and flame resistance; polymers from the para isomer are noted for high tensile strength and high modulus.

o-Phenylenediamines react with most functional groups to give cyclic compounds. Therefore bis-*o*-phenylenediamines, ie, tetraamines, are required for polymer formation. For example, polybenzimidazoles are obtained from 4,4′-oxybis-(1,2-benzenediamine) [26776-59-7], or 4,4′-sulfonylbis-(1,2-benzenediamine) [13224-79-8], and dicarboxylic acids.



Polyquinoxalines can be obtained in a similar fashion using bis-1,2-diketones (see Heat-resistant polymers).

4. Production

The *m*-phenylenediamines are easily obtained by dinitrating, followed by catalytically hydrogenating, an aromatic hydrocarbon. Thus, the toluenediamines are manufactured by nitrating toluene with a mixture of sulfuric acid, nitric acid, and 23% water at 330°C which first produces a mixture (60:40) of the ortho and para mononitrotoluenes. Further nitration produces the 80:20 mixture of 2,4- and 2,6-dinitrotoluene. Catalytic hydrogenation produces the commercial mixture of diamines which, when converted to diisocyanates, are widely used in the production of polyurethanes (see Amines, aromatic, diaminotoluenes) (22).

The ortho and para isomers are obtained by catalytically hydrogenating the corresponding nitroanilines, made by heating the chloronitrobenzene with aqueous ammonia at about 450°C under pressure. These isomers can also be prepared by heating the corresponding dichlorobenzenes with aqueous ammonia at 210°C under pressure in the presence of a copper salt (23).

N-Phenyl-*p*-phenylenediamine [101-54-2], can be manufactured by heating aniline with *p*-chloronitrobenzene in the presence of a copper salt and catalytically hydrogenating the nitro group (24, 25). The preparation of *p*-nitrodiphenylamine has been improved by the reaction of the formamide of aniline with *p*-chloronitrobenzene in the presence of potassium carbonate at 165°C (26). Alternatively, diphenylamine can be *N*-nitrosated and then rearranged to 4-nitrosodiphenylamine [156-10-5] with anhydrous hydrogen chloride (27) followed by reduction. Commercial antiozonants are prepared by reductively alkylating this diamine. A novel route to these antiozonants is the acid catalyzed self-condensation of nitrosobenzene to give *p*-nitrosodiphenylhydroxylamine [28548-57-4] followed by reductive alkylation (28).

The *N,N*′-diphenyl-*p*-phenylenediamine is prepared by heating hydroquinone with aniline in the presence of phosphoric acid (29). *N,N*′-di-2-naphthalenyl-*p*-phenylenediamine is made from *p*-phenylenediamine and 2-naphthol.

United States production of phenylenediamines is shown in Table 3 (30). Production of both the *m*- and *p*-phenylenediamines are not reported since they are produced captively for use in the manufacture of polyamides. However, aromatic polyamide plant capacity is about 30,000 t/yr.

Table 3. United States Production of Phenylenediamine Derivatives, t[a]

Year	2,4- and 2,6-Toluene diisocyanate (80/20)	*N*-Substituted *p*-phenylenediamines
1987	323,416	35,760
1986	301,589	32,680
1984	300,858	26,283
1982	252,195	24,057
1980	266,509	24,716
1975	282,138[b]	33,550
1971	85,274[b]	25,816
1967	40,160[b]	21,641

[a] United States International Trade Commission, Synthetic Organic Chemicals.
[b] Calculated from reported toluenediamine production volumes.

5. Health and Safety

Like aniline, phenylenediamines may be toxic. *p*-Phenylenediamine causes irritation to the pharynx and larynx, and bronchial asthma, but dermatitis is the most common toxic effect. Appropriate substitution of *p*-phenylenediamine, generally on the nitrogen with phenyl or larger alkyl groups, significantly reduces its toxicity. Thus most commercial antioxidants and antiozonants show minimal skin sensitizing effects (31). The American Conference of Government Industrial Hygienists (1983/84) has set a TWA exposure limit at 0.1 mg/m^3 and an “immediately dangerous to health” level of 25 mg/m^3 (32). Correlation between structure and carcinogenicity of 23 phenylenediamines has been reviewed (33) and the toxicity test results of 22 compounds have been tabulated (34).

6. Uses

The largest volumes of phenylenediamines are used for the production of polymers, primarily polyurethanes, where the diisocyanates of toluenediamines (meta isomer) are used. For the manufacture of polyamides both meta and para isomers are used. Another significant use for *p*-phenylenediamines is as antioxidants and antiozonants for elastomers, plastics, and petroleum products. The *N*-alkyl-*N*′-aryl-*p*-phenylenediamines are by far the most commonly used and represent the bulk of the volume of the *N*-substituted *p*-phenylenediamines reported in Table 3. Some *N,N*′-dialkyl compounds are also still used as antiozonants, but they oxidize more rapidly and lose activity sooner. The *N,N*′-diaryl-*p*-phenylenediamines are used primarily as antioxidants, especially where copper and other harmful metals might be present. *N,N*′-Dinaphthalenyl-*p*-phenylenediamine is especially effective in this application. The *N,N*′-diphenyl compound has also been used as an anti-ozonant for neoprene rubber. The excellent reducing capability of these para diamines accounts for their use in these applications. For the same reason, they are also used in color photography and their diazonium salts are also used as photographic chemicals. The oxidation of *p*-phenylenediamines in the presence of amines and phenols is used to manufacture dyes. Many permanent hair dyes are based on the oxidation of *p*-phenylenediamines. Semipermanent hair colorants can be based on all three isomers of phenylenediamine.

Phenylenediamines are used in a variety of other applications, such as corrosion inhibitors, cross-linking agents for epoxy resins, toners for electrostatic image development (35), and to improve wrinkle resistance of cellulose acetate fibers (36).

The applications for *o*-phenylenediamines are limited but are useful for forming heterocyclic compounds and as analytical reagents for identifying a variety of functional groups.

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Related Articles

Urethane polymers; Heat-resistant polymers; Amines, aromatic, diaminotoluenes; Polyamides; Polyimides; High performance fibers; Azo dyes; Sulfur dyes; Azine dyes