Kirk-Othmer Encyclopedia of Chemical Technology.

AMINES, AROMATIC, DIARYLAMINES

Diarylamines are compounds that have two aromatic groups and one hydrogen atom attached to nitrogen. Diphenylamine (DPA), or *N*-phenylbenzenamine [122-39-4], is the most commercially significant diarylamine. It was first prepared by Hofmann in 1863 by destructive distillation of triphenylmethane dyes. Today, it is manufactured by heating aniline by itself, or with phenol, and with an acid catalyst at high temperatures. It is used as a stabilizer for nitrocellulose propellants. When alkylated, diphenylamine finds its largest application as an antioxidant and stabilizer for oils, greases, polymers, and elastomers. Diarylamines that contain other functional groups, such as hydroxyl or amino, are useful dye intermediates, antiozonants, hair dyes, and color photography intermediates.

1. Physical Properties

Selected physical properties for representative diarylamines are given in Table 1. The solubility of DPA in water (1) is given by:

$$\log c = 1.5786 - 1571\ T^{-1}$$

where c is the concentration of DPA in mol/L. The solubility at 10, 15, 20, 25, and 30°C is 1.06, 1.35, 1.75, 2.11, and 2.61×10^{-4} mol/L, respectively.

Diphenylamine is a weak base, $K_b = 9 \times 10^{-4}$. Dilute acids are used to separate DPA from primary aromatic amines, such as aniline, $K_b = 4 \times 10^{-10}$. Diphenylamine hydrochloride [537-67-7] is stable in the presence of 7.5% or stronger hydrochloric acid, but dissociates in more dilute solutions.

2. Reactions

2.1. C-Alkylation

Since para-alkylated derivatives of DPA are widely used in large volumes as antioxidants (qv), the most important reaction of DPA is the acid catalyzed reaction with olefins (2, 3). Alkylation is carried out by adding the olefin to a mixture of DPA and an acid catalyst, such as $AlCl_3$ or an acidic clay, at 120–140°C. Most low cost olefins, mixtures of olefins, and dienes have been used in reactions with DPA. The common commercial alkylated diphenylamines are derived from isobutylene, diisobutylene, styrene, or α-methylstyrene. Diisobutylene primarily produces mono- and di-para tertiary octyl derivatives since steric hindrance significantly slows the alkylation at the ortho position. Thus, only a small amount of tri-substituted product is obtained. Less hindered olefins, eg, styrene, which give a secondary alkyl group, produce proportionally larger amounts of tri

Table 1. Physical Properties of Diarylamines

Diarylamine	CAS Registry Number	Formula	Mp, °C	Bp, °C[a]
diphenylamine	[122-39-4]	$C_{12}H_{11}N$	53	302
2-methyldiphenylamine	[1205-39-6]	$C_{13}H_{13}N$	41	175(2.93)
3-methyldiphenylamine	[1205-64-7]	$C_{13}H_{13}N$	27.5	
4-methyldiphenylamine	[620-84-8]	$C_{13}H_{13}N$	88	
4-(1,1-dimethylethyl) diphenylamine	[4496-49-5]	$C_{16}H_{19}N$	67	139(0.05)
4-octyldiphenylamine	[4175-37-5]	$C_{20}H_{27}N$	48	152(0.03)
4,4′-bis(1,1-dimethylethyl) diphenylamine	[4627-22-9]	$C_{20}H_{27}N$	110	
4,4′-bis(1-phenylethyl) diphenylamine	[60160-25-0]	$C_{28}H_{27}N$		
4,4′-bis(1-methyl-1-phenylethyl)diphenylamine	[10081-67-1]	$C_{30}H_{31}N$	101	
4,4′-dioctyldiphenylamine	[101-67-7]	$C_{28}H_{43}N$	102	
2,2′-diethyldiphenylamine	[64653-59-4]	$C_{16}H_{19}N$		
2,2′-bis(1-methylethyl) diphenylamine	[64653-45-8]	$C_{18}H_{23}N$		
2,4,4′-tris(1-methyl-1-phenylethyl)diphenylamine	[17419-19-1]	$C_{39}H_{41}N$	122	
4-hydroxydiphenylamine	[122-37-2]	$C_{12}H_{11}NO$	73	200(1.33)
4,4′-dimethoxydiphenylamine	[101-70-2]	$C_{14}H_{15}NO_2$	103	
N-phenyl-1-naphthylamine	[90-30-2]	$C_{16}H_{13}N$	62	244(16)
N-[4-(1-methyl-1-phenylethyl) phenyl]-1-naphthylamine	[17418-49-4]	$C_{25}H_{23}N$	92	
N-phenyl-2-naphthylamine	[135-88-6]	$C_{16}H_{13}N$	108	395
N-[4-(1-methyl-1-phenylethyl) phenyl]-1-(1-methyl-1-phenylethyl)-2-naphthylamine	[17418-51-8]	$C_{34}H_{33}N$	122	
di-6-chrysenylamine	[64743-18-6]	$C_{36}H_{23}N$	314	
N-nitrosodiphenylamine	[86-30-6]	$C_{12}H_{10}N_2O$	68	
N,N′-diphenyl-*p*-phenylenediamine	[74-31-7]	$C_{18}H_{16}N_2$	152	200(0.07)
N,N′-di-2-naphthyl-*p*-phenylenediamine	[93-46-9]	$C_{26}H_{20}N_2$	234	
9*H*-carbazole	[86-74-8]	$C_{12}H_9N$	245	
9,10-dihydro-9,9-dimethyl acridine	[6267-02-3]	$C_{15}H_{15}N$	137	
10*H*-phenothiazine	[92-84-2]	$C_{12}H_9NS$	193	
8-octyl-10*H*-phenothiazine	[b]	$C_{20}H_{26}NS$	118	

[a] At 101.3 kPa unless otherwise indicated in kPa in parentheses. To convert kPa to mm Hg, multiply by 7.5.

[b] CAS Registry Number not assigned.

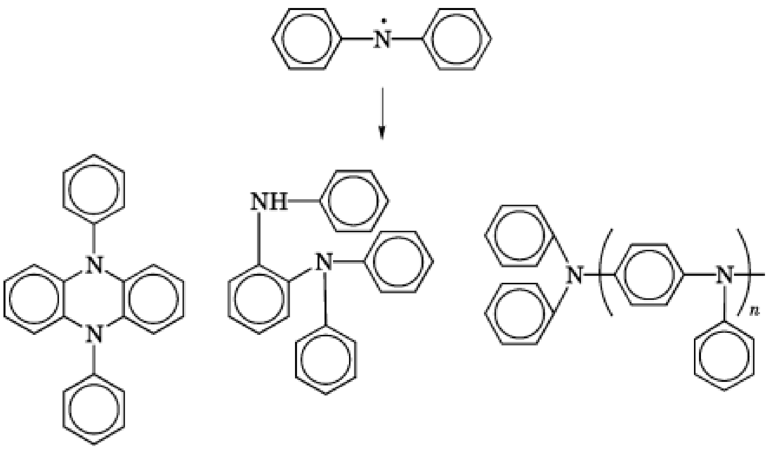
and tetra substituted DPA. Alkylation with various diolefins leads to the formation of higher molecular weight, polymeric products (4).

Acetone also reacts with diphenylamine, in the presence of acid, to form a variety of condition-dependent products (5). Excess amine and a small amount of strong acid catalyst at 100–150°C give 2,2-[4,4′-(dianilino)diphenyl]-propane [2980-26-9] (6). With a large amount of hydrochloric acid at 250°C in the presence of excess diphenylamine, the main product is 9,9-dimethylacridan [6267-02-3].

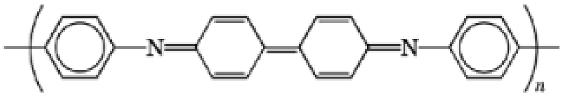
Diphenylamine can be alkylated exclusively in the ortho positions by reacting with an olefin in the presence of aluminum diphenylamide (7), which can be readily obtained by heating DPA with powdered aluminum, or more easily by treating sodium diphenylamide with $AlCl_3$. Ethylene is more reactive than propylene, which in turn is more reactive than isobutylene. For a typical reaction, a small amount of the amide is generated in a DPA melt and ethylene is introduced under pressure (5–30 MPa) at 200–400°C. The absorption of ethylene stops after about 30 min and 2,2′-diethyldiphenylamine is obtained in 95% yield. With propylene only a 25% yield of the 2,2′-diisopropyldiphenylamine is obtained.

2.2. Oxidation

Diarylamines are widely used as antioxidants primarily because they react with and destroy chain propagating peroxy radicals. The first product formed is a long-lived but generally not isolable aminyl radical (8). These radicals can react with other peroxy radicals or couple through the nitrogens, or at the ortho or para positions of the aromatic rings, to give dimers and high molecular weight oligomers such as the following (9).



Thus, *N,N,N′,N′*;-tetraphenylhydrazine [632-52-0], 5,10-dihydro-5,10-diphenylphenazine [3665-72-3], and *N,N,N′*-triphenyl-1,2-benzenediamine [29325-54-0] are oxidation products of DPA. The permanent stain caused by these compounds is in part due to the formation of the following highly conjugated, polymeric products which are insoluble:



For antioxidant activity, the reaction of aminyl radicals with peroxy radicals is very beneficial. The nitroxyl radicals formed in this reaction are extremely effective oxidation inhibitors. Nitroxides function by trapping chain-propagating alkyl radicals to give hydroxylamine ethers. These ethers, in turn, quench chain propagating peroxy radicals and in the process regenerate the original nitroxides. The cyclic nature of this process accounts for the superlative antioxidant activity of nitroxides (see Antioxidants). Thus, antioxidant activity improves with an increase in stability of the aminyl and nitroxyl radicals. Consequently, commercial DPA antioxidants are alkylated in the ortho and para positions to prevent undesirable coupling reactions.

Although aminyl radicals are stable towards oxygen, they can oxidize other aromatic amines, phenols and thiols (10), and regenerate the diarylamine. Thus, mixtures of phenols and diarylamines frequently show better antioxidant activity than either one alone. This is called synergism.

Nitroxyl radicals of diarylamines can also be obtained on oxidation with hydrogen peroxide in the presence of vanadium ions. Resonance helps stabilize these radicals. For example, the nitroxide from 4,4′-dimethoxydiphenylamine [63619-50-1] is stable for years, whereas the radical from the unsubstituted diphenylamine cannot be isolated. Substitution in the ortho and para positions also increases the stabilities of these nitroxides by inhibiting coupling reactions at these sites. However, they are not as stable as the sterically hindered tetramethylpiperidyl radical.

2.3. Miscellaneous Reactions

The *N*-hydrogen atom of diphenylamine is reactive and readily replaced by deuterium by treating with C_2H_5OD. The addition of acid catalyzes the exchange of the hydrogen atoms on the ring system (11).

Electrophilic substitution reactions of diarylamines are easily accomplished since the amino group activates the aromatic ring. Thus, DPA reacts with bromine or chlorine to form the 2,2′4,4′ tetrahalo derivative; nitration usually produces the trinitro compound.

Hydrogenation of diarylamines yields dialicyclic amines, but hydrogenolysis of the carbon-nitrogen bond also occurs. Dehydrogenation of DPA yields carbazole and alkyl derivatives of DPA give acridines. Dehydrogenation with sulfur gives phenothiazines (12).

Since diarylamines are relatively weak bases, they react relatively slowly, or not at all, in typical amine reactions. Diarylamines undergo Mannich reactions with a variety of active hydrogen compounds (13). Formaldehyde reacts with DPA to give *N,N,N′,N′*;-tetraphenylmethylenediamine [21905-92-0]. In the presence of strong acids, this rearranges to the ring-substituted product 4,4′-(dianilino)-diphenylmethane and higher polydiarylamines. Nitrous acid and other nitrosating agents easily give *N*-nitroso derivatives. These compounds can be rearranged to the ring-substituted DPA. Thus, *N*-nitrosodiphenylamine [86-30-6], with excess anhydrous HCl in alcohol, at low temperatures, gives 4-nitrosodiphenylamine [156-10-5] in excellent yields (14). Nitrosyl chloride and DPA, under the same conditions, lead directly to the 4-nitrosodiphenylamine. Water must be avoided in the reaction since it reacts with nitrosyl chloride.

Diarylamines do not react with carbon disulfide, whereas dialkylamines readily form dithiocarbamates. However, *N,N′*-diaryldithiocarbamates can be prepared from metal salts of diarylamines and carbon disulfide (15). They are more stable than dialkyldithiocarbamic acids, eg, *N,N′*;-diphenyldithiocarbamic acid [7283-79-6], mp 142°C. Similarly, various metal salts of DPA react with carbon dioxide and an epoxide to give the β-hydroxyalkyldiphenylcarbamates (16).

Diarylamines can be *N*-alkylated with anhydrides and acyl halides or *N*-alkylated with alkyl halides, alkyl sulfates, and tri-*n*-alkylphosphites.

Diphenylamine derivatives of alkyl–aryl gallium, germanium, phosphorus, and silicon are known (17), eg, pentaphenylgermanamine [64653-46-9].

3. Manufacture

Diarylamines are manufactured by the self-condensation of a primary aromatic amine in the presence of an acid, or the reaction of an arylamine with a phenol, at high temperatures.

Diphenylamine is manufactured by the self-condensation of aniline in the presence of a small amount of a mineral acid, such as anhydrous hydrogen chloride, or Lewis acids, such as ferrous chloride or ammonium bromide.

$$2\ C_6H_5NH_2 \xrightarrow[300^\circ C]{HCl} (C_6H_5)_2NH + NH_3$$

Thermodynamic analysis of this reaction shows favorable energy relations (18). The standard free energy of formation of DPA is 310.5 kJ/mol (74.2 kcal/mol) (19).

The reaction may be carried out in a corrosion-resistant apparatus fitted with an appropriate fractionating column. Here, the ammonia is separated from the aniline and removed from the reaction. The pressure is controlled to maintain the temperature near 300°C. When conversion reaches 50–60%, the excess aniline is distilled and the pure diphenylamine is then isolated by vacuum distillation. Yields range from 83 to 95% (20, 21).

The vapor-phase conversion of aniline to DPA over a solid catalyst has been extensively studied (18, 22). In general, the catalyst used is pure aluminum oxide or titanium oxide, prepared under special conditions (18). Promoters, such as copper chromite, nickel chloride, phosphoric acid, and ammonium fluoride, have also been recommended. Reaction temperatures are usually from 400 to 500°C. Coke formed on the catalyst is removed occasionally by burning. In this way, conversions of about 35% and yields of 95% have been reported. Carbazole is frequently a by-product.

The second major route to diarylamines is the condensation of an aromatic amine with a phenol. Aniline [62-53-3], phenol [108-95-2], and 3.5% phosphoric acid at 325°C gives a 50% yield of DPA (23). Apparently, this reaction involves the addition of aniline to the keto form of the phenol. Thus, naphthols and hydroquinone are more reactive and give higher yields of product. This is the preferred route to *N*-phenyl-2-naphthylamine, 4-hydroxydiphenylamine, and *N,N′* diphenyl-*p*-phenylenediamine (24).

A process for the production of DPA from phenol and ammonia has been reported (25). Typically, the reaction is carried out continuously in a fixed-bed reactor using an acidic alumina catalyst at 300°C–420°C. The first product formed is aniline which is subsequently converted to DPA. Consequently, the reaction can be carried out to simultaneously produce DPA and aniline, in any desired ratio, simply by varying the molar ratios of phenol (and aniline) in the reactor feed stream.

Aromatic amines also react with halobenzenes to produce diarylamines. DPA forms when aniline and chlorobenzene are heated together. This reaction takes on commercial significance when the halobenzene is activated by an electron withdrawing group. The reaction of *p*-nitrochlorobenzene with aniline in the presence of copper cyanide and potassium carbonate at 200°C has been used to manufacture *p*-nitrodiphenylamine [836-30-6] (26). 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 (27). The *p*-nitrodiphenylamine can be easily reduced to *p*-aminodiphenylamine, a precursor to several commercial *p*-phenylenediamine antiozonants (qv). These compounds can also be prepared by the self-condensation of nitrosobenzene to *p*-nitrosodiphenylhydroxylamine [28548-57-4] followed by reductive alkylation (28).

According to the U.S. International Trade Commission's Synthetic Organic Chemicals, Production and Sales, 1987, the three manufacturers of diphenylamine are Rubicon, Inc., Aristech Chemical Corp., and Uniroyal Chemical Co. No production figures have been given since 1974, but U.S. production in the range of 5,000–10,000 t/yr appears reasonable.

4. Laboratory Procedures

Specific diarylamines not easily obtained by the above methods can be prepared by the Ullmann (29) and Chapman (30) reactions. For example, *m*-chloroaniline reacts with *o*-chlorobenzoic acid in the presence of potassium carbonate and a catalytic amount of a copper salt to give 2-[(3-chlorophenyl)amino]benzoic acid [13278-36-9], which is then decarboxylated on heating to 3-chlorodiphenylamine [101-17-7].

The Chapman synthesis makes use of an arylamine and a phenol. The arylamine is converted to the benzamide which then reacts with phosphorus pentachloride to give the *N*-aryl-α-chlorobenzylideneimine. Reaction with the sodium salt of a phenol gives the arylimino ether which rearranges to the benzamide on heating. Hydrolysis with alcoholic potassium hydroxide gives the diarylamine in 80% yield. Benzamides hindered in the 2,6-positions are resistant to hydrolysis and cannot be prepared in this way. Alternatively, benzamides have been prepared by reaction of *p*-bromophenol with anilides, which are then hydrolyzed to diarylamines (31).

An additional method utilizes the reaction of metallic salts of primary aromatic amines with aryl halides, apparently via a benzyne intermediate. Thus, the sodium salt of *p*-toluidine reacts with *p*-bromotoluene to give a mixture containing di-*p*-tolylamine [620-93-9], *m,p*-ditolylamine [62121-57-7], and aminoditolyls (32).

Catalytic dehydrogenation of dicyclohexylamine [101-83-7], *N*-cyclohexylaniline [1821-36-9], or *N*-cyclohexylidineaniline [10592-26-4] with Pt/Al_2O_3 at 375°C gives 40% carbazole [86-74-8] and 20% DPA (33). The catalytic dehydrogenation of imines derived from cyclohexanones and aromatic amines can also be used to prepare diarylamines (34). Certain unsaturated imines can be isomerized and aromatized to diarylamines. Thus, the imine of carvone and aniline $C_{16}H_{19}N$ [68388-27-2] when treated with rhodium chloride in ethanol containing potassium carbonate at 100°C gives a 50% yield of 2-methyl-5-isopropyldiphenylamine [68388-29-4] (35).

5. Analysis

Diarylamines may be identified by melting point. Chromatographic techniques, such as hplc, gc, and tlc, are especially useful for separating and identifying diarylamines. Infrared, uv, nmr, x-ray and mass spectroscopy are also used. Diarylamines are also used as analytical reagents in the detection of various materials, eg, *N,N′*-[iminobis(9,10-dihydro-9,10-dioxo-4,1-anthracenediyl)]bis-benzamide [128-79-0] for boron, germanium, selenium, and tellurium and 2,2′4,4′,6,6′-hexanitrodiphenylamine [131-73-7] has been used for potassium. As a spot test, diphenylamine in concentrated sulfuric acid with oxidizing agents produces a blue color.

6. Toxicity

Diphenylamine in the basic diet of rats at 0.5–1.5% inhibits growth and causes liver and kidney disorders (36). Industrial poisoning by diphenylamine has been encountered and appears clinically as bladder symptoms, tachycardia, hypertension, and skin problems (37). There is no federal standard for permissible exposure limits in air, but the American Conference of Government Industrial Hygienists (1983/84) has adopted a Time Weighted Average value of 10 mg/m^3 and set a Short Term Exposure Limit of 20 mg/m^3. The alkylated diphenylamines, used as antioxidants, have much higher molecular weights and are relatively nonvolatile.

N-Nitrosodiphenylamine can act as a nitrosating agent for other amines with all the consequences thereof (see *N*-Nitrosamines).

As with the parent aromatic hydrocarbons, diarylamines based on polycyclic aromatic amines also tend to be more harmful. Thus, *N*-phenyl-2-naphthylamine [135-88-6] (PBNA) metabolizes in the body to produce small amounts of 2-naphthylamine, a known carcinogen (37). ACGIH has designated PBNA to be an “industrial substance suspect of carcinogenic potential for man.”

7. Uses

Diarylamines are of the greatest industrial importance as stabilizers and antioxidants (qv) for polymers, stabilizers for explosives, polymerization inhibitors, and in dyes. Today, the use of these materials as antioxidants is essentially limited to derivatives of diphenylamine since *N*-phenyl-2-naphthylamine is no longer used.

Diarylamines function as rubber antioxidants by breaking the peroxidative chain reactions leading to rubber deterioration. Nearly all commercial synthetic rubbers (see Elastomers, synthetic), including neoprene, butyl, styrene–butadiene, and the acrylonitrile–butadiene rubbers, can be protected with about 1–2% of an alkylated diphenylamine. DPA itself is not used as a rubber antioxidant. An objectionable feature of these antioxidants is that they cause discoloration and staining which limits their use to applications where this is not important.

The 9,9-dimethylacridan formed in the reaction between diphenylamine and acetone, besides functioning as an antioxidant, also improves the flex life of rubber vulcanizates since it forms a more stable nitroxyl radical than the alkylated diphenylamines.

N-Aryl-*p*-phenylenediamines can be considered to be 4-amino substituted diarylamines. However, phenylenediamines are significantly different than diarylamines. *p*-Phenylenediamines possess antiozonant activity, deactivate prooxidative metal ions, and improve flexing properties while diarylamines do not. Nevertheless, DPA is the starting material used for the production of *N*-alkyl-*N*′-aryl-*p*-phenylenediamine antiozonants (see Amines, phenylenediamines).

Diphenylamine antioxidants are also widely used to stabilize roofing asphalts, lubricating greases, silicone enamels, polyamides, acetal resins, and other hydrocarbons. They have been used as corrosion inhibitors in glycol heat-exchanger fluids (antifreezes) and as volatile corrosion inhibitors for steel (see Corrosion and corrosion inhibitors). They also stabilize sulfur trioxide.

In explosives, diphenylamine stabilizes cellulose nitrate by reacting with nitrogen oxides (see Explosives and propellants). The products formed include *N*-nitrosodiphenylamine and mono and polynitro derivatives.

The addition of 2,2′,4,4′,6-pentanitro-6′-methyldiphenylamine [64653-47-0] to seawater precipitates potassium (38). Aromatic amines, especially aminotetrahydronaphthalenes and their *N*-aryl derivatives, are efficient flotation agents for quartz. The use of DPA for image formation in films has been patented (39, 40). Diarylamines are used as intermediates (41) for azo, sulfur, oxidative base, triarylmethane, oxazine, nitro, and safranine dyes (see Dyes and dye intermediates).

Diphenylamine inhibits the development of scald disease during prolonged cold storage of apples and pears (42–45). It prolongs the fresh appearance of cut snapdragons (46), controls weather fleck in tobacco, inhibits algae formation, and shows growth inhibitory activity in potatoes (47).

Diphenylamine has shown activity against the body louse, chiggers, housefly, and, as the chloro derivative, against the red spider mite. Diarylamines have also been reported to have antiradiation activity (48).

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