Kirk-Othmer Encyclopedia of Chemical Technology.

BIPHENYL AND TERPHENYLS

Biphenyl (diphenyl, phenylbenzene) and terphenyl are the lowest members of a family of polyphenyls in which benzene rings are attached one to another in a chainlike manner, $C_6H_5(C_6H_4)_mC_6H_5$. Many higher polyphenyls are known (1), but only biphenyl and the terphenyls are of commercial significance. Some lower boiling quaterphenyl isomers, $C_{24}H_{18}$, are sometimes included in products obtained by high vacuum distillation of crude terphenyls. Structures of biphenyl, $C_{12}H_{10}$, and the three terphenyl isomers, $C_{18}H_{14}$, are shown in Table 1.

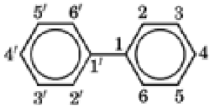
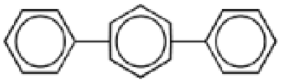
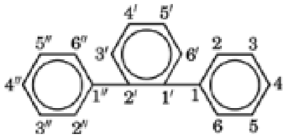
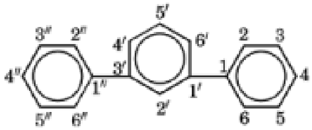
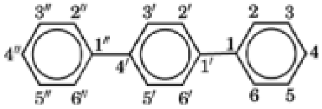
Biphenyl was first reported in 1862 (2) and identified in 1867 (3) as the main product obtained by passing benzene vapors through a hot tube. In a 1874 investigation (4) of the higher boiling products of benzene pyrolysis, benzene vapors were passed through a glowing iron pipe, and, in addition to biphenyl, *m*- and *p*-terphenyl were isolated. The ortho-isomer was identified in 1927 (5). Shortly thereafter, biphenyl and (coincidently) terphenyls became commercially available by a dehydrocondensation process in which benzene vapor was passed through molten lead baths at 750°C (6). Although the lead pots have long since been replaced by modern gas or electrically heated tube reactors, vapor-phase dehydrocondensation of benzene [71-43-2] is still an important commercial route to biphenyl; it is the method of choice for production of terphenyls.

1. Physical Properties

Pure biphenyl is a white crystalline solid that separates from solvents as plates or monoclinic prismatic crystals. Commercial samples are often slightly yellow or tan in color. Similarly, pure terphenyls are white crystalline solids whereas commercial grades are somewhat yellow or tan. Physical and chemical constants for biphenyl and the three isomeric terphenyls are given in Tables 2 and 3, respectively.

Individual terphenyl isomers are not ordinarily isolated in pure form but are most often utilized as isomer mixtures. During the late 1950s and 1960s, terphenyls and partially hydrogenated derivatives, because of their radiation resistance and good thermal stability, were regarded as promising organic coolants for nuclear reactors. Many physical property studies of biphenyl and the terphenyls, both as pure compounds and in various mixtures, were carried out. Extensive collections of physical property data which attest to the high degree of activity engendered by the nuclear application are available (7, 12, 22). As interest in organic-cooled reactors declined, industrial heat-transfer applications remained the main outlet for terphenyls. Although the latter was served primarily by partially hydrogenated terphenyl mixtures, Monsanto for many years marketed the unhydrogenated terphenyl precursor having a composition of approximately 2–10% *o*-terphenyl, 45–49% *m*-terphenyl, and 25–35% *p*-terphenyl with 2–18% higher polyphenyls. The product's high liquidus temperature (about 145°C) hampered its utility as a heat-transfer medium. A more useful composition containing less *p*-terphenyl and more low melting quaterphenyls is now commercially available. Some physical properties of this low melting polyphenyl mixture are given in Table 4.

Table 1. Biphenyl and the Terphenyls

Common name	CAS name	CAS Registry Number	Structure
biphenyl	1,1′-biphenyl	[92-52-4]	
	terphenyl	[26140-60-3]	
o-terphenyl	1,1′:2′,1″-terphenyl	[84-15-1]	
m-terphenyl	1,1′:3′,1″-terphenyl	[92-06-8]	
p-terphenyl	1,1′:4′,1″-terphenyl	[92-94-4]	

2. Chemical Properties

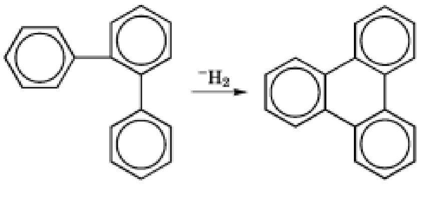
Biphenyl and terphenyls may be regarded as substituted benzenes that undergo acylation, alkylation, halogenation, nitration, sulfonation, and other reactions common to benzene (qv). The points of initial attack on chlorination, nitration, and sulfonation of biphenyl occur at the 2- and 4-positions; the latter predominates. Alkylation by olefins, which affords the most commercially important class of biphenyl derivatives, takes place largely at the 4-position. Alkyl substituents in the 4-position can reorganize under the influence of strong Lewis acids to a mixture of 3- and 4-substituted biphenyls in which the 3-alkyl isomer often predominates (23). Acid catalyzed alkylation of biphenyl can also be effected by alkyl transfer from a polyalkylbenzene. This reaction is most facile when the alkyl group is ethyl (24). Considerable attention has been focused on developing catalysts and conditions for the selective diisopropylation of biphenyl in the 4,4′-positions (25, 26). The resulting 4,4′-diisopropylbiphenyl [18970-30-4] can be oxidized to the corresponding [1,1′-biphenyl]-4,4′-dicarboxylic acid [787-70-2] (27), regarded as a promising monomer for heat-resistant and liquid crystal polymers (28).

Table 2. Physical Properties of Biphenyl

Property	Value				Reference
melting point, °C	69.2				7
freezing point commercial grades, °C	68.5–69.4				8
boiling point at 101.3 kPa^a, °C	255.2 ± 0.2				7
specific gravity, solid					
d^{20}	1.041				9
d^{15}	0.991				9
critical properties					
temperature, °C	515.7				10
pressure, MPa^b	4.05				10
density, g/mL	0.314				10
flash point, °C	113.0				11
fire point, °C	123.0				11
autogenous ignition temperature, °C	560.0				12
heat of combustion, kJ/mol^c	6243.2				13
heat of fusion, kJ/mol^c	18.60				12
	Temperature, °C				
	100°C	200°C	300°C	350°C	
vapor pressure, kPa^a		25.43	246.8	558.06	9
liquid density, g/mL	0.970	0.889	0.801	0.751	9
heat capacity, J/g^c	1.786	2.129	2.468	2.640	9
heat of vaporization, J/g^c	397.0	343.0	284.7	251.0	9
viscosity, mm^2/s (= cSt)	0.98	0.43	0.24		11
thermal conductivity liquid, W/(cmK)^d	13.39	11.92	10.46	9.75	14

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J to cal, divide by 4.184.
[d] To convert W/(cm·K) to (cal·cm)/(s·cm^2·°C), divide by 4.184.

Terphenyls, like biphenyl, undergo the usual reactions of aromatic hydrocarbons. The ortho- and para-isomers nitrate initially at the 4-position whereas the meta-isomer nitrates at the 4′-position (29). *Ortho*- and *m*-terphenyl can be isomerized to the para-isomer (30, 31). *o*-Terphenyl, refluxed for a short time with aluminum chloride in benzene, gives 94% meta-isomer. More drastic isomerization conditions afford conversions of up to 84% para-isomer. Isomerization in the other direction also can be forced. Japanese workers (32) claim a 29% yield of *o*-terphenyl by slow fractionation of *o*-terphenyl from a 64:36 mixture of *m*- and *p*-terphenyl heated at 530–535°C over a Y-type zeolite catalyst. Currently, isomerizing the more abundant meta- and para-isomers is the more attractive direction, since *o*-terphenyl, because of its low melting point, is the most useful of the three isomers for heat-transfer applications. Commercially, partial reduction to a complex mixture of dicyclohexylbenzenes, biphenylcyclohexanes, and phenyldicyclohexane is the most important reaction that the terphenyls undergo. Under strongly dehydrogenating conditions, *o*-terphenyl cyclizes to triphenylene [217-59-4] (33). The latter is a minor (1.5%) impurity present in crude polyphenyls prepared by pyrolytic dehydrocondensation of benzene.



o-terphenyl triphenylene

Table 3. Physical Properties of Pure Terphenyl Isomers

Property	*Ortho-*	*Meta-*	*Para-*	Reference
melting point, °C	56.2	87.5	212.7	15
boiling point at 101.3 kPa[a], °C	332.0	365.0	376.0	16
heat of vaporization of 101.3 kPa[a] at bp, kJ/kg[b]	253.0	279.0	272.0	16
flash point, °C	171.0	206.0	210.0	17
fire point, °C	193.0	229.0	238.0	17
auto ignition temperature, °C	530.0	555.0	555.0	12
vapor pressure, kPa[a]				
93°C	0.01172	0.00165		16
204°C	2.834	0.827		16
315.6°C	64.40	27.3		16
426.7°C	439.9	240.6		16
density of liquid, g/L				
93°C	1022.0	1039.0	solid	18
204°C	935.0	958.0	solid	18
315.6°C	842.0	871.0	879.0	18
heat capacity of liquid, kJ/kg[b]				
93°C	1.007	0.970		16
315°C	1.300	1.298		16
398.9°C	1.400	1.397	1.116	16
viscosity of liquid, mPa·s(= cP)				
100°C	4.34	3.87	solid	19
225°C	0.66	0.78	0.74	19
300°C	0.30	0.40	0.43	19
350°C			0.32	19
thermal conductivity of liquid, W/(m·K)[c]				
100°C	0.1316	0.1347		19
150°C	0.1266	0.1306		19
210°C	0.1206	0.1356	0.1359	19
260°C			0.339	19
heat of vaporization, J/g at 252°C	280.0	298.0	305.0	20
heat of fusion, kJ/kg[b]	55.2	73.7	146.5	
critical temperature, K	891.0	927.0	926.0	19
critical pressure, MPa[d]	3.903	3.503	3.330	21

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert J to cal, divide by 4.184.
[c] To convert W/(m·K) to (cal·cm)/(s·cm^2·°C), divide by 418.4
[d] To convert MPa to psi, multiply by 145.

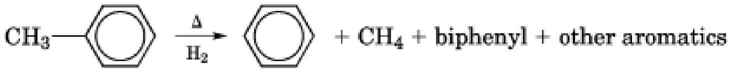
3. Manufacture

Biphenyl has been produced commercially in the United States since 1926, mainly by The Dow Chemical Co., Monsanto Co., and Sun Oil Co. Currently, Dow, Monsanto, and Koch Chemical Co. are the principal biphenyl producers, with lesser amounts coming from Sybron Corp. and Chemol, Inc. With the exception of Monsanto, the above suppliers recover biphenyl from high boiler fractions that accompany the hydrodealkylation of toluene [108-88-3] to benzene (6). Hydrodealkylation of alkylbenzenes, usually toluene, C_7H_8, is an important source of benzene, C_6H_6, in the United States. Numerous hydrodealkylation (HDA) processes have been developed. Most have the common feature that toluene or other alkylbenzene plus hydrogen is passed under pressure through a tubular reactor at high temperature (34). Methane and benzene are the principal products formed. Dealkylation conditions are sufficiently severe to cause some dehydrocondensation of benzene and toluene molecules.

Table 4. Physical Properties of a Commercial[a] Terphenyl–Quaterphenyl Mixture

Property	Value
composition	~65% terphenyls ~45% *ortho-* ~50% *meta-* ~5% *para-* ~35% quaterphenyls
appearance	soft solid melting to yellow liquid
melting range, °C	40–70
flash point, °C[b]	204.0
fire point, °C[b]	232.0
autogenous ignition temperature, °C	538.0
kinematic viscosity, mm^2/s (= cSt) at 50°C	97.9
coefficient of thermal expansion per °C	8.8×10^{-4}
heat of vaporization, J/g[c]	
boiling range at 6.66 kPa[d], °C	239
10% over	255.0
90% over	340.0

[a] Monsanto Product Bulletin IC/FP-215A, 1990.
[b] Cleveland Open Cup.
[c] To convert J to cal, divide by 4.184.
[d] To convert kPa to mm Hg, multiply by 7.5.



Approximately 1 kg of biphenyl per 100 kg of benzene is produced (6). Because of the large scale, HDA operations provide an ample source of crude biphenyl from which a technical grade of 93–97% purity can be obtained by distillation (35). Zone refining or other crystallization techniques are required to further refine this by-product biphenyl to the ≥99.9% purity required for heat-transfer applications.

High purity biphenyl is currently produced by Monsanto in the United States and United Kingdom by direct dehydrocondensation of benzene. Terphenyls are also obtained from the higher boiling polyphenyl by-products that accompany the biphenyl (36). Foreign producers making biphenyl and terphenyls by the benzene dehydrocondensation route include Bayer (Germany), Nippon Steel (Japan) and Russia. Industrial production is carried out in gas or electrically heated tubular reactors at 700–800°C. Residence times are on the order of 10–30 seconds. Some control on the ratio of biphenyl to terphenyl can be exercised by adjusting temperature and flow rates and by recycling biphenyl. However, there is little control over the ratio of *ortho*-, *meta*-, and *para*-terphenyl isomers produced.

Since the thermal dehydrocondensation proceeds by a free-radical mechanism (37), various radical-forming promoters like acetone, ethanol, or methanol have been found useful in improving conversion of benzene to condensed polyphenyls. In the commercial dehydrocondensation process, benzene and some biphenyl are separated by distillation and recycled back to the dehydrocondensation step. Pure biphenyl is then collected leaving a polyphenyl residue consisting of approximately 4% *o*-terphenyl, 44% *m*-terphenyl, 25% *p*-terphenyl, 1.5% triphenylene, and 22–27% higher polyphenyl and tars. Distillation of this residue at reduced pressure affords the mixed terphenyl isomers accompanied by a portion of the quaterphenyls present. Depending on intended use, more or less of the quaterphenyl fraction is included with the terphenyl cut.

Batchwise fractional distillation can be used to adjust the ratio of isomers in the mixture. For example, the heat-transfer composition of Table 4 is obtained by collecting all of the *ortho*- some of the *meta*-, and excluding most of the *para*-terphenyl present in the natural mixture. Economics and considerations of melting point depression favor inclusion of lower melting quaterphenyl isomers.

Pure *o*-terphenyl can be obtained by fractional distillation. To obtain high purity *m*- or *p*-terphenyl, the appropriate distillation fraction has to be further purified by recrystallizing, zone refining, or other refining techniques. Currently, little demand exists for pure isomers, and only a mixture is routinely produced. Small amounts of acetone, ethanol, or methanol are used to promote dehydrocondensation, and as a result, minor amounts of methyl- or methylene-substituted polyphenyls accompany the biphenyl and terphenyls produced. For most purposes, the level of such products ($<1\%$) is so small that their presence can be ignored. For applications requiring removal of these alkyl-polyphenyl impurities, an efficient process for their oxidative destruction has been described (38).

4. Shipping

By-product biphenyl is usually sold as a dye carrier in the molten state in tank truck or tank car lots. Grades of higher purity are also sold in the molten state or as flakes in 22.7 kg bags.

Biphenyl is defined as a toxic chemical under, and subject to, reporting requirements of Section 313 of Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986 and 40 CFR, Part 372 under the name biphenyl. It is identified as a hazardous chemical under criteria of the OSHA Hazard Communication Standard (29 CFR 1910.1200).

The small amount of mixed terphenyls that are sold as such, are shipped in the form of flaked solids in 22.7 kg multiwall bags. The U.S. freight classification is Plastics, synthetic other than liquid, NOIBN. Like biphenyl, mixed terphenyls fall under the hazardous chemical criteria of the OSHA Hazard Communication Standard (29 CFR 1910.1200).

The terphenyl–quaterphenyl heat-transfer medium (Table 4), sold as Therminol 75 heat-transfer fluid, is shipped in drums, tank car, or tank truck lots. Its U.S. freight classification is Heat-Transfer Media, NOIBN. The material does not require a DOT hazardous material label, but does fall under the hazardous chemical criteria of the OSHA Hazards Communications Standard (19 CFR 1910.1200).

5. Economic Aspects

Reliable estimates of annual production of biphenyl in the United States are difficult to obtain. The 1990 figure is probably on the order of 16 million kg/yr of which about half is derived from hydrodealkylation sources. About 10% of the biphenyl derived from HDA sources is consumed, as 93–95% grade, in textile dye carrier applications. The remainder is used for alkylation or upgraded to $\geq 99.9\%$ grades for heat-transfer purposes. Essentially all of the high purity biphenyl produced by dehydrocondensation of benzene is used as alkylation feedstock or is utilized directly in heat-transfer applications.

The actual capacity for biphenyl production in the United States is not reported, but considering the flexibility for recovery from hydrodealkylation sources and a shrinking dye carrier market, production capacity for HDA-grade biphenyl substantially exceeds demand. Requirements for high grade biphenyl dropped precipitously following termination of polychlorinated biphenyl production in 1972. During the ensuing decade, benzene dehydrocondensation plants were downsized, and terphenyls became the primary dehydrocondensation product. More recently, the trend has gradually reversed because of expanding heat-transfer and alkylation markets. In 1988 an expansion of production capability was announced by Monsanto (39).

Biphenyl prices vary widely depending on grade, quantities purchased, and special contract arrangements. In 1991 the U.S. published price for 99.9% biphenyl was \$1.40 to \$1.63 per kg depending on quantity and packaging (40). Lower purity HDA-grades run roughly half this price.

Table 5. Toxicological Properties of Biphenyl

Measurement	Value	Reference
Airborne exposure limits		
OSHA PEL	0.2 ppm 8 h TWA	(42, 43)
ACGIH TLV	0.2 ppm 8 h TWA	(42, 43)
Toxicity data		
oral, g/kg	rat LD_{50} = 2.4	42
	rat LD_{50} = 3.28, rabbit = 2.41	44
dermal, g/kg	rabbit LD_{50} = >5.01	42
inhalation, mg/L	rat LC_{50} = >0.2	42
eye irritation	(rabbit) 2.8 on a scale of 110	42
skin irritation	(rabbit, 24 h) 0.3 on a scale of 8	42

As in the case of biphenyl, current worldwide production figures for terphenyls are not readily obtainable, but the volume is probably around 6.8–8.2 million kg/yr. Currently, most of the terphenyl produced is converted to a partially hydrogenated form. U.S. production of terphenyls has remained steady at several thousand metric tons per year over the past decade. The 1991 small lot price for mixed terphenyls was about $3.89/kg whereas the specially fractionated heat-transfer-grade terphenyl–quaterphenyl mixture sold as Therminol 75 heat-transfer fluid was priced around $6.93/kg. Partially hydrogenated mixed terphenyls were priced in the $6.05–7.48/kg range depending on quantity and grade.

6. Specifications, Analytical Control, and Storage

Biphenyl, terphenyl, and their alkyl or hydrogenated derivatives generally serve markets where price and performance, rather than composition, is the customer's primary concern. Performance standards for heat-transfer applications are usually set by the fluid supplier. The biphenyl–diphenyl oxide eutectic (26.5% biphenyl, 73.5% DPO) represents a special case. This composition has become a widely recognized standard vapor-phase heat-transfer medium. It is sold throughout the world under various trademarks. In the United States, Dow (Dowtherm A) and Monsanto (Therminol VP-1) are the primary suppliers. Alkylated biphenyls and partially hydrogenated terphenyls serving the dielectric and carbonless copy paper dye solvent markets likewise are sold primarily on the basis of price and performance characteristics jointly agreed on by producer and user.

Because the thermal stability of the materials is generally high, gas–liquid chromatography (glc) is by far the most widely used analytical method employed for analysis and quality control in the manufacture of biphenyl, terphenyls, and their derivatives. In the 1980s, reverse-phase high performance liquid chromatography (hplc) became increasingly useful in the analysis of complex high molecular weight polyphenyl mixtures (41), but it is not routinely employed.

Biphenyl and mixed terphenyls as well as their normally liquid alkyl and partially hydrogenated derivatives are commonly stored in the liquid or molten state. The products are noncorrosive; mild steel equipment usually suffices for handling.

7. Health and Safety Factors

Although biphenyl and the terphenyls fall under the hazardous chemical criteria of the OSHA Hazard Communications Standard, the products themselves are fairly low in toxicity and do not constitute a serious industrial hazard. Some relevant exposure and toxicity data are summarized in Tables 5 and 6.

Table 6. Toxicological Properties of Terphenyls

Measurement	Value	Reference
Airborne exposure limits		
OSHA PEL	ceiling = 1.0 ppm (9 mg/m^3)	(45, 46)
ACGIH TLV	ceiling = 0.5 ppm (5 mg/m^3)	(45, 46)
Toxicological data		
oral, g/kg		
mixed isomers	rat LD$_{50}$ = >5	45
ortho-isomer	rat LD$_{50}$ = 1.9	47
meta-isomer	2.4	47
para-isomer	>10	47
dermal, g/kg	rabbit LD$_{50}$ = >12.5 (mixed isomers)	45
eye irritation	(rabbit 24 h) 0.7 on a scale of 110	45
skin irritation	(rabbit 24 h) 0.0 on a scale of 8	45

Because biphenyl is often transported in the molten state, a moderate fire hazard does exist under these circumstances. Biphenyl, with a flash point of 113°C, has a lower flammability limit of about 0.6% (by volume) at the flash point to an upper limit of 5.8% at 166°C (42). Dust explosions are a hazard when vapors from a hot liquid surface condense in air in a confined space.

8. Environmental Considerations

The widespread use of biphenyl and methyl-substituted biphenyls as dye carriers (qv) in the textile industry has given rise to significant environmental concern because of the amount released to the environment in wastewater effluent. Although biphenyl and simple alkylbiphenyls are themselves biodegradable (48–50), the prospect of their conversion by chlorination to PCBs in the course of wastewater treatment has been a subject of environmental focus (51–53). Despite the fact that the lower chlorinated biphenyls are also fairly biodegradable (49, 54, 55) continued environmental concern has resulted in decreased use of biphenyl as a dye carrier (see Dyes, environmental chemistry).

Terphenyls in heat-transfer applications are used in relatively smaller quantities with negligible release to the environment. They are sufficiently biodegradable so as not to constitute an environmental threat (56, 57). Some properties important for environmental considerations are summarized in Table 7.

9. Use

In the past, dye carrier applications consumed a significant portion of the biphenyl produced in the United States with heat transfer being a strong but lower volume outlet. A shift away from biphenyl in textile dyeing during the 1980s and a steady growth in the vapor-phase heat-transfer market has caused a reversal of the earlier market positions. The biphenyl and diphenyl ether eutectic is by far the most important biphenyl outlet into the heat-transfer market. The eutectic is sold throughout the world under various trademarks including Dowtherm A (Dow), Therminol VP-1 and Santotherm VP-1 (Monsanto), Diphyl (Bayer), Thermio (ICI), and Therm S-300 (Nippon Steel). The eutectic has a maximum operating temperature of about 400°C. Vapor pressure at this temperature is about 1.1 MPa (11 atm). In seeking heat-transfer fluids capable of 400°C operation, it is often desirable to employ a liquid-phase medium. The terphenyl and quaterphenyl mixture of Table 4 was designed for this purpose. Other lower melting mixtures containing biphenyl, *o*-terphenyl, and

Table 7. Properties of Biphenyl and Terphenyls of Environmental Importance

Property	Value	Reference
vapor pressure at 25°C, Pa[a] biphenyl	1.3	
water solubility at 25°C, mol/dm^3		
biphenyl	4.57×10^{-5}	58
o-terphenyl	5.38×10^{-6}	58
m-terphenyl	6.65×10^{-6}	58
p-terphenyl	7.80×10^{-6}	58
aeration stripping, 4 h COD[b] reduction, %		
biphenyl	89.0	
biphenyl BOD at 20°C	79.0	
octanol–water partition coefficient, log *P*		
biphenyl	4.1	59
p-terphenyl	6.03	60
biphenyl bioconcentration ratio	438 ± 48	

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

[b] COD = Chemical oxygen demand.

m-terphenyl in combination with various phenyl ethers have been proposed (38, 61) for high temperature solar heat collection systems.

10. Derivatives

Historically, polychlorinated biphenyls (PCBs) and to a lesser extent polychlorinated terphenyls (PCTs) were the most important derivatives of the respective polyphenyls. When they came to be recognized as serious environmental contaminants, production ceased in the early 1970s. These products are now of significance primarily because of their environmental aftereffects (62). Much environmental research and governmental regulations stem therefrom (see Chlorocarbons and chlorohydrocarbons, toxic aromatics).

Short-chain alkylated biphenyls are the principal biphenyl derivatives in commercial use. They are generally produced by liquid-phase Friedel-Crafts alkylation of biphenyl with ethylene, propylene, or mixed butenes. A series of mixed ethylated biphenyl heat-transfer fluids (trademarked Therm S-600, 700, 800) is marketed by Nippon Steel. A mixed diethylbenzene–ethylbiphenyl heat-transfer fluid is also available from Dow (63). Monoisopropylbiphenyl [25640-78-2], largely as a mixture of meta- and para-isomers is produced by Koch Chemical Co. Monoisopropylbiphenyl (MIPB) was selected by Westinghouse (64, 65) as a PCB replacement in capacitors and this is its primary application today. For a time MIPB was also employed as a PCB replacement in pressure sensitive copy paper, but this outlet has since given way to other dye solvents. A similar product consisting of a mixture of *sec*-butylbiphenyl isomers [38784-93-9] (66) is currently the favored dye solvent for pressure sensitive copy paper (67) manufactured in the United States.

Domestic production figures for alkylated biphenyls are not readily available, but the volume is probably in the range of 10–14 million kg/yr with prices at approximately $1.50 per kg.

Ortho- and *para*-phenylphenols are commercially significant biphenyl derivatives that do not involve biphenyl as a starting material. Both are produced as by-products from the hydrolysis of chlorobenzene [108-90-7] with aqueous sodium hydroxide (68). *o*-Phenylphenol, ie, 1,1-biphenyl-2-ol [90-43-7], particularly as its sodium salt, is widely used as a germicide or fungicide. *Para*-phenylphenol [92-69-3] with formaldehyde forms a resin used in surface coatings.

Several functionalized biphenyls either are, or show promise of becoming, commercially significant polymer building blocks. Thus new routes to 4,4′-dihydroxybiphenyl [92-88-6] have been the subject of attention.

In addition to the conventional synthesis via alkali fusion of the 4,4′-disulfonate (69, 70), methods involving 4,4′-diiodobiphenyl [3001-15-8] (71) and the hydroperoxidation of 4,4′-diisopropylbiphenyl (72) are under development. An alternative commercial route to 4,4′-dihydroxybiphenyl, practiced by Dart Industries, involves oxidative coupling of 2,6-di*tert*-butylphenol [128-39-2] followed by dealkylation of the tetraalkylbiphenyl formed. Details of this process have been reviewed (73). 4,4′-Diisopropylbiphenyl can be oxidized to [1,1′-biphenyl]-4,4′dicarboxylic acid [787-70-2] (27) which is also an attractive polyester building block.

Semicommercial production of 3,3′,4,4′-biphenyltetracarboxylic dianhydride [2420-87-3] in the United States has been announced by Occidental Chemical Corp. (74). This polyimide resin intermediate is prepared by dehalogenative dimerization of 4-chlorophthalate salts (75) or by oxidative coupling of phthalate esters (76).

Nearly all of the terphenyls produced both in the United States and abroad are partially hydrogenated to afford a complex hydrocarbon mixture [61788-32-7] in which approximately 40% of the aromatic rings have been reduced. Producers may vary the degree of hydrogenation to some extent as well as the amount of quaterphenyls allowed to accompany the terphenyl feed cut. Economics favor maximum inclusion, but viscosity specifications usually enforce a limit of around 25%. Terphenyls can be hydrogenated over a variety of catalysts with Raney nickel preferred for the commercial process. Hydrogenated terphenyls are produced in the United States and United Kingdom by Monsanto. Other producers include Bayer (Germany), Nippon Steel (Japan), and Russia.

Hydrogenated terphenyls are widely used in industrial heat-transfer systems operating in the 0°C to 340°C range. An application receiving increased attention involves their use as a direct heating medium for the condensation of polyester oligomers to ultrahigh molecular weight polyesters (77). Reduced terphenyls, either alone or in mixtures, are employed as dye solvents by European carbonless copy paper producers. Consumption in this area has declined over the past decade. Hydrogenated terphenyls are also used in certain plasticizer applications,primarily PVC. Minor amounts are sold for various other uses (lubricant, hydraulic, nuclear reactor coolant, etc).

Worldwide production of hydrogenated terphenyls is estimated to be around 9 million kg/yr with demand remaining fairly steady. Current U.S. prices are in the range of $5.50–6.05/kg.

10.1. Safety

Hydrogenated terphenyls are low in toxicity as the following data (78) indicate. Single exposure (acute) studies show:

oral LD_{50} (rat) = >10 g/kg
dermal LD_{50} (rabbit) = >2.0 g/kg
inhalation LC_{50} (rat 4 h) = >4.7 mg/L
eye irritation (rabbit, 24 h) = 0.3 on a scale of 110
skin irritation (rabbit, 24 h) = 0.1 on a scale of 8·

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QUENTIN E. THOMPSON
Monsanto Company

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