Abstract: Pentalene has recently received a considerable amount of attention as a ligand in sandwich-type transition metal complexes. In contrast, dibenzo[a,e]pentalene (hereafter denoted as dibenzopentalene), which is more π-extended than pentalene, has received less attention, despite its potential usefulness as a building block of ladder-type π-conjugated molecules, which have recently received growing interest. However, very recently, several novel efficient methods for the synthesis of dibenzopentalenes have been reported. This review surveys recent advances in the synthesis and reactions of dibenzopentalenes and describes the aromaticity of their ionic species.

Keywords: dibenzopentalene; thermolysis; skeletal rearrangement; reductive cyclization; catalyst; redox reaction

1. Introduction

The parent pentalene has 8π electrons, which indicates its antiaromatic nature, and is very highly reactive, having only been observed using a matrix isolation technique at −196 °C (Chart 1) [1,2]. In contrast, its dianion has 10π electrons and is calculated to have considerable aromaticity [3]. The stable pentalene dianion was first synthesized in 1962 [4,5] and the X-ray crystal structure of its dilithium salt was reported in 1991 [6]. On the other hand, no reports on the generation of a pentalene dication have appeared to date, and its aromaticity is still controversial [3,7]. The pentalene dianions are now widely used as ligands of sandwich-type transition metal complexes [8-11]. However, the dibenzo[a,e]pentalenes (hereafter denoted as dibenzopentalenes), which are more π-extended than the pentalenes have received less attention despite their potential usefulness as building blocks of ladder-type π-conjugated molecules, which are of growing recent interest (Figure 1). The main reason for this
is a limited number of methods for the synthesis of dibenzopentalene frameworks, even though synthesis of a dibenzopentalene was first reported in 1912 [12]. However, very recently, efficient and unique methods for the synthesis of dibenzopentalenes together with reports of their reactivity have successively appeared. It is therefore time to briefly survey the recent advances in the synthesis and reactions of dibenzopentalenes and to discuss the aromaticity of their derivatives.

Figure 1. Pentalene and Dibenzo[a,e]pentalene.

2. Early Studies on the Preparation of Dibenzopentalenes

The first synthesis of dibenzopentalenes 1a-b was reported by Brand in 1912 [12]. The key starting compound was diphenylsuccindanedione 2 [13-15], which was synthesized from diphenylsuccinic acid. Treatment of 2 with phenylmagnesium bromide and p-tolylmagnesium bromide followed by an addition of ammonium chloride afforded the corresponding diols 3a and 3b, respectively (Scheme 1) [12]. Diols 3a and 3b were treated with formic acid to provide dibenzopentalenes 1a and 1b. This method could be applied to introduce other aryl or alkyl groups, such as o-anisyl [16], p-anisyl [16], methyl [17] and ethyl [17] groups, leading to the formation of dibenzopentalenes 3c-3f (Scheme 1).

Scheme 1. Early Studies on the Preparation of Dibenzopentalenes from Diphenylsuccindanedione 2.

The parent dibenzopentalene 1g was first synthesized from dihydrodibenzopentalene 4a, which was prepared from diphenylsuccindanedione 2 via tetrachlorodibenzopentalene 4b (Scheme 2) [18]. Diphenylsuccindanedione 2 reacted with phosphorus pentachloride to afford 4b [19,20], which was treated with zinc to provide 4a [20]. Treatment of 4b with bromine followed by silver acetate provided the parent dibenzopentalene 1g in 59% yield (Scheme 2) [18].
Dibromodibenzopentalene 1h was prepared by the thermolysis of dibenzotricyclic tetrabromide 5 [21] and by the reaction of 5 with sodium iodide (Scheme 3) [22]. Bromination of tetrahydrodibenzopentalene 6 followed by dehydrobromination also afforded 1h (Scheme 3) [22].

Scheme 3. Preparation of the Dibromodibenzopentalene 1h.

3. Preparation of Dibenzopentalenes by Thermolysis

Thermolysis, such as the flash vacuum pyrolysis (FVP) technique, is sometimes a very powerful tool for the creation of rigid π-frameworks through somewhat unexpected and complex reaction pathways.

Bis(pentachlorophenyl)acetylene 7 was heated at 350 ºC for 45 min to afford perchloro-1,2,3-triphenylnaphtalene 8 (42%) as a main product with perchloro-2,3,8-triphenylbenzofulvene 9 (31%) and perchlorodibenzopentalene 10 (1%) (Scheme 4) [23]. Prolonged heating of 7 for 2 h revealed an increase of the yield of 10 (23%) and a decrease of the yields 9 (10%): hence, dibenzopentalene 10 was formed via 9.

Scheme 4. Thermolysis of Perchloro-1,2,3-triphenylnaphtalene 8.

Flash vacuum pyrolysis of diphenylbutadiyne 11 at 1120 ºC/0.03 Torr gave a pyrolysate (22% mass recovery), which consisted of dibenzopentalene 1g (19%), fluoranthene 12 (59%), acephenanthrylene 13 (13%), aceanthrylene 14 (2%) and unreacted 11 (7%) (Scheme 5) [24].
Flash vacuum pyrolysis of 3-phenyl naphthalene-1,2-dicarboxylic anhydride \(15\) at 900 \(^\circ\)C/0.04 mmHg also gave dibenzopentalene \(1g\) (95\%) and a plausible mechanism for the formation of \(1g\) was proposed (Scheme 6) [25].

**Scheme 6. Flash Vacuum Pyrolysis of 3-Phenyl Naphthalene-1,2-Dicarboxylic Anhydride 15.**

Flash vacuum pyrolysis of 9,10-bis[(methoxysilyl)methyl]anthracene \(16\) at 550 \(^\circ\)C/10\(^{-3}\) mmHg also gave dibenzopentalene \(1g\) (48\%), and a very complicated mechanism was proposed (Scheme 7) [26].

**Scheme 7. Flash Vacuum Pyrolysis of 9,10-Bis[(methoxysilyl)methyl]anthracene 16.**

Benzo[\(b\)]biphenylene \(16\), benzo[\(b\)]fluorenone \(17\) and 5,12-naphthacene quinone \(18\) were also heated in the gas phase to provide dibenzopentalene \(1g\) and fluoranthene \(12\), and the ratios of \(1g\) to \(12\) were dependent on the reaction temperature (Scheme 8) [27].

Thermolysis is indeed efficient for the preparation of dibenzopentalenes. However, it needs a special apparatus: hence, it is rather difficult to carry out. Moreover, it is difficult to prepare functionalized dibenzopentalenes using thermolysis.
Scheme 8. Flash Vacuum Pyrolysis of Benzannulated Compounds.

![Scheme 8](image)

4. Preparation of Dibenzopentalenes from Dibenzocyclooctene Derivatives through Skeletal Rearrangement

Anionic dibenzocyclooctene derivatives are known to undergo skeletal rearrangements to afford the corresponding dibenzopentalenes.

Treatment of 5,6,11,12-tetrabromodibenz[a,e]cyclooctatetraene 19 with alkyllithiums followed by an addition of phenyllithium and electrophiles provided dihydrodibenzopentalenes 4c-4i (Scheme 9) [28]. However, when compound 19 was treated with phenyllithium without a treatment with electrophiles, 5,10-diphenyldibenzopentalane 1a was also obtained.

Scheme 9. Reactions of 5,6,11,12-Tetrabromodibenz[a,e]cyclooctene 19 with Lithium Reagents.

![Scheme 9](image)

A similar method starting from dibenzocyclooctadiyne 20 was very recently reported [29]. Dibenzocyclooctadiyne 20 reacted with alkyllithiums to provide the corresponding anionic intermediates 21, which underwent isomerization to anionic dibenzopentalenes 22. The reactions were terminated with electrophiles to afford dibenzopentalenes 1h-1s in very good yields (61–78%) (Scheme 10) [29].
To introduce an aryl group to the dibenzopentalene skeleton, treatment of 20 with butyllithium followed by iodine afforded iodo-derivative 1t, which reacted with arylboronic acids and aryltributylstannanes through Suzuki-Miyaura and Migita-Kosugi-Stille coupling reactions, respectively, to provide the corresponding aryl derivatives 1u-1y in good yields (50–70%) (Scheme 11) [29].

Scheme 11. Preparation of Aryl-substituted Dibenzopentalenes.

5. Preparation of Dibenzopentalenes through Reductive Cyclization

The intramolecular cyclization reactions of o-substituted phenylacetylenes are of considerable use for the preparation of benzannulated five-membered ring compounds, such as indenes, indoles, benzofurans and benzothiophenes [30,31]. A very sophisticated application of this methodology to prepare dibenzopentalene skeletons was very recently reported by Yamaguchi [32]. Reduction of o,o’-bis(arylcyanobenzy)diarylacetylenes 23 with lithium naphthalenide produced dibenzopentalenes 1 (8–25% yields) together with 5,10-dihydroxy-5,10-dihydrodibenzopentalenes 4 (29–52% yields) (Scheme 12). Since dihydroxy derivative 4k reacted with lithium naphthalenide to afford the corresponding dibenzopentalenes 1a in 49% yield (Scheme 13), Li₂O was eliminated from dilithium alkoxide intermediate 24.
Scheme 12. Reductive Cyclization of o,o'-Bis(arylcarbonyl)diphenylacetylenes 23.

Another example of reductive cyclization of a phenylacetylene to form a dibenzopentalene is rather unexpected. We recently reported the reduction of phenyl(tri-i-propylsilyl)acetylene 25a with lithium providing dilithium dibenzopentalenide 26a as well as 1,4-dilithio-1,3-butadiene 27a, which were treated with iodine to afford the corresponding dibenzopentalene 1aa (8%) and 1,4-diiodo-1,3-butadiene 28a (28%), respectively (Scheme 14) [33]. Since phenylsilylacetylenes are usually reduced by lithium to afford 1,4-dilithio-1,3-butadienes [34,35], the formation of dilithium dibenzopentalenide 26a is surprising and unprecedented. However, the reduction of phenyl(t-butyldimethylsilyl)acetylene 25b with lithium produced only the corresponding 1,4-dilithio-1,3-butadiene 27b: thus, the reaction mode is quite sensitive to bulkiness of the silyl substituent of phenylsilylacetylene, even though the reason for this is still unclear.
6. Preparation of Dibenzopentalenes in the Presence of Catalysts

Catalytic reactions for the preparation of dibenzopentalenes have also been reported. In early studies, the key starting compound was 1,2-bis(phenylethynyl)benzene (29a), treatment of which with PtCl$_4$ in benzene afforded a Pt-complex of dibenzopentalene 1bb, an unstable compound that converted to 1bb during purification (Scheme 15) [36,37]. The yield of 1bb was 85%. This method was later applied for the preparation of dibenzopentalenes 1cc-1ff (Scheme 15) [38]. When PdCl$_2$ was used as a catalyst, a Pd-complex of 1bb was isolated and treatment of the resulting complex with triphenylphosphine provided 1bb, even though the yield was very low. A mixture of H$_2$PtCl$_6$·6H$_2$O and Aliquat 336® (Aliquat = methyltrioctylammonium chloride) was also used as a catalyst for the preparation of 1bb with 80% yield [39]. When the reactions were carried out in the presence of dialkyl acetylenedicarboxylates, the corresponding adducts 1gg-1ii were obtained (25–36% yields) together with 1bb (Scheme 16) [40].

**Scheme 15.** Formation of Dibenzopentalene from 1,2-Bis(phenylethynyl)benzene (29a).

**Scheme 16.** Cyclization of 1,2-Bis(phenylethynyl)benzene (29a) in the Presence of Dialkyl Acetylenedicarboxylates.

The cyclization reactions of 1,2-bis(phenylethynyl)benzenes to afford dibenzopentalenes were surprisingly catalyzed by tellurium (Scheme 17) [38]. Heating of 29a with a catalytic amount of tellurium in pentachloroethane (PCE) under reflux provided dibenzopentalene 1jj in 61% yield through a halogen transfer reaction (Scheme 17). When 29a was heated with a catalytic amount of tellurium in tetrabromoethane at 170 °C, the corresponding bromodibenzopentalene 1kk was obtained in 6% yield (Scheme 18) [38]. Treatment of 29b with a catalytic amount of tellurium in PCE under reflux produced a 1:1 mixture of 1ll and 1mm in 79% yield. Likewise, 29c reacted in PCD in the presence of a catalytic amount of tellurium to afford an 1:1 mixture of 1nn and 1oo in 83% yield.
Scheme 17. Cyclization of 1,2-Bis(phenylethynyl)benzenes Catalyzed by Tellurium in Pentachloroethane.

![Scheme 17](image)

Scheme 18. Cyclization of 1,2-Bis(phenylethynyl)benzenes Catalyzed by Tellurium in Tetrabromoethane.

![Scheme 18](image)

Two phenylacetylenes, one of which has a halogen atom and the other of which has a Bu₃Sn group were coupled in the presence of CsF, tBu₃P and Pd₂(db₃)₃ to give dibenzopentalenes (Scheme 19) [41]. The coupling reaction of 30a and 31a under the reaction conditions shown in Scheme 19 provided dibenzopentalene 1a in 61% yield. A crossover coupling reaction of 30b and 31a under the same conditions afforded homocoupled products 1a (20% yield) and 1qq (trace), as well as the crossover-coupled product 1pp (40% yield), suggesting that the homocoupling reaction of 31a would proceed.

Heating of 31a and 31b afforded 1a and 1qq, respectively in very high yields with 2 equivalents of hydroquinone, Cs₂CO₃ and CsF in the presence of catalytic amounts of tBu₃P and Pd₂(db₃)₃ in 1,4-dioxane at 135 °C (Scheme 20) [41]. This method could be applied for the preparation of a variety of dibenzopentalenes (55–72% yields) (Scheme 21) [41]. The most striking feature of this catalytic system is that a heteroaromatic analog 34 of a dibenzopentalene was able to be synthesized.

Scheme 19. Coupling of Two Acetylenes in the Presence of CsF, tBu₃P and Pd₂(db₃)₃.
Scheme 20. Homocoupling of Acetylenes with hydroquinone, Cs₂CO₃ and CsF in the Presence of tBu₃P and Pd₂(dba)₃.


Another catalytic synthesis of a dibenzopentalene from 2-halophenylacetylene was carried out using Pd(PPh₃)₂Cl₂ and CuI (Scheme 22) [42]. Heating of a mixture of 2-iodophenylacetylene 35 with Pd(PhCN)Cl₂, PPh₃ and CuI in toluene and diisopropylamine at 90 °C provided dibenzopentalene 1tt in 67% yield (Scheme 22). Although this system is simpler than that in Scheme 21, no further applications for the synthesis of dibenzopentalenes have been reported.

Scheme 22. Preparation of Dibenzopentalene from 2-Iodophenylacetylene.
Being inspired by this catalytic system, an extremely simple synthesis of dibenzopentalenes from 2-bromoethynylbenzenes was reported. Treatment of 2-bromoethynylbenzene 25d with an equivalent of Ni(PPh₃)₂Cl₂ and 1.5 equivalents of Zn at 80 °C produced dibenzopentalene 1uu in 41% yield (Scheme 23) [43]. Reaction of 25d with Ni(cod)₂ and PPh₃ at 50 °C afforded Ni complex 36, which was transformed into 1uu at 80 °C. In the initial step, a generated intermediate Ni(0) complex Ni(PPh₃)₂ therefore underwent oxidative addition to 25d to give 36. The yield of 1uu was improved to 46% in the presence of Ni(cod)₂, PPh₃ and Zn at 110 °C. This method enabled the synthesis of a variety of dibenzopentalenes (13–24% yields) (Scheme 24 and 25) [43]. It is noted that the electronic nature of substituents on the aromatic rings did not affect the formation of dibenzopentalenes.

**Scheme 23.** Preparation of Dibenzopentalene with Ni(0) Catalyst.

![Scheme 23](image)

**Scheme 24.** Preparation of Functionalized Dibenzopentalenes with Ni(0) Catalyst.

![Scheme 24](image)

**Scheme 25.** Preparation of Diaryl-substituted Dibenzopentalenes with Ni(0) Catalyst.

![Scheme 25](image)

A unique two-step synthesis of a dibenzopentalene was also reported recently. The two starting compounds 37 [44] and 38 were prepared from commercially available 3,5-dimethoxybenzaldehyde in
five and three steps, respectively. Compounds 37 and 38 were subjected to standard Heck reaction conditions to afford indene derivative 39 in 53% yield (Scheme 26) [45]. Oxidative cyclization of 39 occurred in the presence of FeCl₃ to provide dibenzopentalene 1ab in 38% yield (Scheme 26) [45].

**Scheme 26.** Preparation of Dibenzopentalene through a Coupling Reaction of Stilbene and Tolane.

Starting from diketone 2, thienyl-substituted dibenzopentalenes were synthesized by the classical method (Scheme 27) [15]. Diketone 2 reacted with thienyllithium or thienylmagnesium bromide to afford the corresponding adducts, which were treated with acid to provide thienyl-substituted dibenzopentalenes 1ac-1ae. When a cyclic voltammetric analysis of 1ac was carried out, the growth of a new redox system was observed upon scanning between −1.0 and 1.2 V and the electrode was modified, suggesting polymerization of 1ac on the electrode. The anodic study of the modified electrode between −1.0 and 1.5 V revealed that the original species on the modified electrode was further modified, perhaps due to intramolecular cyclization or polymerization through the benzene moiety (Scheme 28) [15]. The band gap of the resulting polymer was estimated to be about 2.2 V.
8. Aromaticity of Dibenzopentalenes

To evaluate aromaticity of dibenzopentalene, current densities in \( \pi \)-systems induced by external magnetic fields were calculated [46]. The current pattern of dibenzopentalene has three distinct regions, and the central paratropic ring current in the two five-membered rings is bordered by diatropic ring currents in the two benzene rings. The paratropic ring current in the central five-membered rings is derived from two \( \pi \)-electrons in the HOMO, whereas the diatropic benzene ring currents arise from several orbitals that lie just below the HOMO. This regional character of the current patterns is consistent with NICS [47] values for individual rings: the NICS values of the five- and six-membered rings are 7.4 and \(-9.8 \) ppm, respectively.

Scheme 27. Preparation of Thienyl-substituted Dibenzopentalenes from Diketone 2.

Scheme 28. Electrochemical Polymerization of Dibenzopentalene 1ac.
9. Ionic Species of Dibenzopentalenes

Redox behavior of dibenzopentalenes is of considerable interest because two-electron oxidation and reduction of dibenzopentalenes afford the corresponding 14π dications and 18π dianions, respectively, which are both expected to be aromatic.

Treatment of dibenzopentalenes 1e and 1g with excess SbF₅ in SO₂ClF resulted in dark green and violet-purple solutions, respectively, attributed to the formation of dications 40 (Scheme 29) [48,49]. The ¹H NMR spectra of the resulting solutions showed considerable downfield resonances, compared with those of the starting 1e and 1g, suggesting that dications 40 are aromatic.

Scheme 29. Formation of Dications of Dibenzopentalenes.

Dianion 26b of the parent dibenzopentalene 1g was synthesized by the reaction of dihydrodibenzopentalene 4a with butyllithium (Scheme 30) [48,49]. Although the H1 and H9 resonated upfield, compared with those of 1g, the other protons on the benzene rings were deshielded, suggesting diatropic ring current over the perimeter of the framework. It is therefore concluded that 26b should be regarded as a peripheral aromatic dianion. Dianion 26c of dibenzopentalene 1e was synthesized by the reaction of 1e with lithium, and a considerably aromatic character was observed (Scheme 30) [48,49].

Scheme 30. Formation of Dianions of Dibenzopentalenes.

Very recently, the first report on the molecular structure of a dianion of a dibenzopentalene has appeared (Scheme 14) [33]. The X-ray crystallographic analysis of 26a revealed that the five-membered rings contain nearly equalized C–C bond lengths, whereas a slight bond alternation in those of the six-membered ring is found, suggesting preferable aromatic delocalization in the five-membered ring over benzenoid delocalization. Similar trends were also found in some benzannulated anions [50-56]. Dianion 26a was also synthesized by the reaction of the corresponding dibenzopentalene 1aa with lithium (Scheme 31) [57]. Oxidation of 26a occurred by treatment with iodine to provide 1aa.
Dications and dianions are formed through the cation radical and the anion radical, respectively. The synthesis of cation radicals $41a$ and $41b$ of dibenzopentalenes were accomplished by the reactions of dibenzopentalenes $1e$ and $1g$ with aluminum trichloride, the formation of which was evidenced by ESR spectroscopy (Scheme 32) [58]. Respective anion radicals $42a$ and $42b$ of $1e$ and $1g$ were synthesized by the reactions of $1e$ and $1g$ with potassium (Scheme 33) [58].

Subsequent challenging tasks are to characterize molecular structures of cation radicals, anion radicals and dications of dibenzopentalenes.

10. Reactions of Dibenzopentalenes

Although a variety of dibenzopentalenes can now be synthesized, their reactivity has been explored very little. Very recently, unique reactions of a dibenzopentalene were reported. Dibenzopentalene $1aa$ reacted with methyllithium to quantitatively produce lithium 5-methyldibenzopentalenide $42$, the structure of which was established by X-ray crystallographic analysis (Scheme 34) [57]. Since 6,6-dimethylfulvene derivative reacted with methyllithium to give the corresponding lithium $t$-butylcyclopentadienide [59], $1aa$ reacted with methyllithium as a fulvene to give $43$. The C–C bond lengths of the cyclopentadienyl anion moiety differ slightly, in contrast to dilithium dibenzopentalenide $26a$ [33], which displays no alternation of the C–C bonds in the five-membered ring. The six-membered ring adjoining the anionic five-membered ring also has different C–C bond lengths.
lengths in the anion. On the other hand, remarkable alternation of the C–C bonds is found in the cyclopentadiene ring of 43. Nucleus-Independent-Chemical-Shifts (NICS) values calculated at 1.0 Å above (−12.5 ppm) and below (−12.9 ppm) the cyclopentadienide ring [47,60] of the model compound of 43 are negative, suggesting aromatic character of the cyclopentadienide ring.

Scheme 34. Reaction of Dibenzopentalene 1aa with Methyllithium.

Dibenzopentalene 1aa reacted with bromine and iodine to provide the corresponding dihalodibenzopentalenes 1af and 1ag in very high yields (Scheme 35) [57]. Dihalodibenzopentalenes would be good starting compounds for further functionalization of dibenzopentalenes.

Scheme 35. Reaction of Dibenzopentalene 1aa with Halogens.

11. Summary and Outlook

Dibenzopentalenes have long been known, and their unique redox behavior leading to 14\pi and 18\pi aromatic species is well established. However, their chemistry is still limited because of the lack of versatile synthetic methods. Very recently, there have been reported several efficient methods for the synthesis of a wide variety of dibenzopentalenes, together with their unique reactions. It is therefore appropriate to cultivate a new chemistry of dibenzopentalenes, which would be applied as building blocks of new \pi-extended sandwich complexes and redox-active materials.

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