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Iptycenes Chemistry

From Synthesis to Applications

Springer

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Preface

In 1942, triptycene was synthesized by Bartlett and his coworkers, which was served as the first and simplest member of iptycene family. In the next 40 years, iptycene family had not attracted much attention until Hart first formally proposed the concept "iptycene" in 1981. Since then, iptycene chemistry has truly established. Iptycenes are a class of aromatic compounds with arene units fused to bicyclo[2.2.2]octatriene bridgehead system. These unique three-dimensional rigid structures make them promising candidates for more and more applications in molecular machines, supramolecular chemistry, material science, coordination chemistry, sensor applications in the last decade. Iptycene chemistry is walking into its golden age with great opportunities and challenges. However, during the 70 years of iptycene chemistry, there were only some relevant reviews. Thus, a comprehensive book, which reviews the retrospections and prospects of iptycenes chemistry, is not only an urgent need but also of great significance. In addition, this year also marks the 70th anniversary for the development of iptycene chemistry (1942–2012). This current situation inspired us to prepare this comprehensive book *Iptycene Chemistry: From Synthesis to Applications*.

Overall, this book contains three parts. Part I includes a brief introduction of the basic naming rules and general properties of iptycenes and their derivatives. Part II details the various methods for synthesis and functionalized reactions of triptycenes, pentiptycenes, other higher iptycenes, heterotriptycenes, and iptycene-based polymers. Chapter 2 aims at the synthetic methods and the reactions of triptycene and its derivatives, as well as the synthesis of the extended triptycenes containing fused rings. In Chap. 3, the synthesis and reactions of pentiptycenes and their derivatives are discussed in details. In addition, the method for the preparation of extended pentiptycenes is also provided. The preparation of the other iptycenes, including the heptipycene, noniptycene, and other iptycene members containing the more complicated framework will be talked about in Chap. 4. According to the different positions of the hetero atom(s), Chap. 5 is divided into three subsections: (1) the bridgehead-substituted heterotriptycenes, (2) heterotriptycenes with heterocycles, and (3) miscellaneous heterotriptycenes and their derivatives. The last chapter (Chap. 6) in this part mainly describes the methods for the preparation of various iptycene-derived polymers. After that, the applications of iptycenes in different areas are discussed in Part III. First, the varied molecular machines capable of mimicking the behaviors of macroscale objects, including gearings, brakes, ratchets, compasses, gyroscopes, wheelbarrows, and the rotaxane-based molecular machines are described in Chap. 7. In Chap. 8, we talk about the iptycene-based materials, involving the long alkyl or alkoxy-substituted triptycenes and iptycenes (and iptycene-based polymers) with the unusual internal free volumes (IFVs) on the applications of liquid crystals. Then, the materials containing good optical and electrical properties, and the porous materials based on iptycene moieties with adsorption and separation capacities are also shown in this chapter. In Chap. 9, we mainly depict the design and synthesis of various novel triptycene- and pentiptycene-derived hosts, and their complexation behaviors with different kinds of guests. Three aspects of iptycenes in self-assembly, including self-assembly in crystal with multiple supramolecular interactions, the construction of self-assembled monolayers with iptycenes and surface modification, and the self-assembly in solution based on the novel iptycene-derived synthetic host, are discussed in Chap. 10. Chapter 11 describes the iptycene molecules served as the building blocks for the metal complexes and the varied and novel complexes with special properties. Then, the varied chemosensors and biosensors based on the iptycene derivatives, especially, the iptycene-based conjugated polymers are discussed in Chap. 12. The varied triptycene-based molecules served as molecular balances to offer the attractive platforms for the study of noncovalent interactions are depicted in details in Chap. 13. Finally, another four applications are shown in Chap. 14, including the different drug activities, especially, antitumor activities of the iptycenes and their derivatives; the iptycenes act as models for Jahn–Teller effect systems and artificial photosynthesis, as well as the iptycenes applied in preparation of carbene. We sincerely hope this book will not only be useful and helpful for the researchers in iptycene chemistry, but can stimulate and facilitate future researches also.

Finally, we would like to acknowledge June Tang, associate editor from Springer, for her kind invitation, and her help and suggestions during the preparation of this manuscript. We also thank Dr. Xiao-Zhang Zhu, Dr. Yi Jiang, Yun Shen, and Ying Han from our research group for their review of the manuscript.

Chuan-Feng Chen
Ying-Xian Ma

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Abbreviations

1D	One dimension
2D	Two dimension
3D	Three dimension
6FDA	4,4-(hexafluoroisopropylidene) diphthalic anhydride
A	Electron acceptor
AFPs	Amplifying fluorescent polymers
Am	Pentyl
AM1 Calculations	Austin Model 1 calculations
BET	Brunauer–Emmett–Teller
Boc	*t*-butyloxy carbonyl
BPAPC	Poly(bisphenol A carbonate)
BQ	Benzoquinone
CAN	Ceric ammonium nitrate
CBPQT	Tetracationic cyclobis(paraquat-*p*-phenylene)
COD (cod)	1,5-cyclooctadiene
Cp	Cyclopentadienyl
CPK	Corey–Pauling–Koltun
D	Electron donor
DATRI	2,6-di-aminotriptycene
DAU	Daunomycin
DB24C8	Dibenzo-[24]crown-8
DB30C10	Dibenzo-[30]crown-10
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	Dicyclohexylcarbodiimide
DCE	1,2-dichloroethane
DCM	Methylene dichloride
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DFT Calculations	Density functional theory calculations
DIBAL-H	Diisobutylaluminium hydride
DIBAH	Diisobutylaluminium hydride
DIPEA	Diisopropylethylamine
DLS	Dynamic light-scattering

DMA	*N*, *N′*-dimethylacetamide
DMAD	Dimethyl acetylenedicarboxylate
DMAP	*N, N*-4-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMF	*N, N*-dimethylformamide
DMS	Dimethyl sulfide
DMSO	Dimethyl sulfoxide
DNA	Deoxyribonucleic acid
DNT	2,4-dinitrotoluene
DR	Dichroic ratio
DTT	Dithiothreitol
EDTA	Ethylene diamine tetraacetic acid
EPR	Electron paramagnetic resonance
ESI-MS	Electrospray ionization mass spectra
FIrpic	Ir^{III} bis(4,6-difluorophenyl-pyridinato)-picolinate
GPC	Gel permeation chromatography
HFIP	Hexafluoro-2-propanol
HMPA	Hexamethyl-phosphoramide
HOPG	Highly oriented pyrolytic graphite
HPLC	High-performance liquid chromatography
IEC	Ion-exchange capacity
IFV	Internal free volume
IMFV	Internal molecular free volume
IR	Infrared spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
K_a	Association constant
LbL	Layer-by-layer
LC	Liquid crystal
LCs	Liquid crystal solutions
LDA	Lithium diisopropylamide
LiDBB	Lithium 4,4′-di-*t*-butylbiphenilide
LIF	Laser-induced fluorescence laser
MALDI-TOF MS	Matrix assisted laser desorption ionization-time of flight mass spectrometry
MCPBA (*m*-CPBA)	*Meta*-chloroperbenzoic acid
MDR	Multidrug-resistant
MOFs	Metal-organic frameworks
MP	Methyl propiolate
MS	Mass spectrometry
NBS	*N*-bromosuccinimide
NMP	*N*-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
o-DCB	1,2-dichlorobenzene
PC	Polycarbonate
PDAC	Poly(diallyldimethylammonium chloride)

PIMs	Polymers of intrinsic microporosity
Pn	Pentacene
PPDs	Poly(*p*-phenylenebuta diynylene)s
PPEs	Poly(phenyleneethynylene)s
PPVs	Poly(phenylene vinylene)s
PS	Polystyrene
PTP	Permeability transition pore
Py	Pyridyl
RH	Relative humidity
ROMP	Ring-opening olefin metathesis polymerization
ROX	Carboxy-X-rhodamine
S_NAr	Nucleophilic aromatic subsititution
SPR	Surface plasmon resonance
STM	Scanning tunneling microscopy
SWCNTs	Single-walled carbon nanotubes
TBA	Tributylamine
TBAF	Tetra-*n*-butylammonium fluoride
TBAF	Tetrabutylammonium fluoride
TEM	Transmission electron microscope
Tf	Trifluoromethanesulfonyl
TFA	Trifluoroacetic acid
T_g	Glass-transition temperature
THF	Tetrahydrofuran
TIPS	Triisopropylsilyl
TLC	Thin-layer chromatography
TMEDA	N, N,N',N'-tetramethylethylenediamine
TMS	Trimethylsilyl
TNT	2,4,6-trinitrotoluene
Tp	9-triptycyl
TPC	Triptycene
TPQ	Triptycene quinone
TP-TCNQ	9,10-dihydro-9,10-*o*-benzeno-1,4-bis(dicyanomethyl-ene)anthracene
Ts (Tos)	*p*-toluenesulfonyl
Upy	Ureidopyrimidinone
UV	Ultraviolet

Part I
Introduction and Background

Chapter 1
Introduction and Background

1.1 Introduction

Iptycenes are a class of aromatic compounds with arene units fused to bicyclo[2.2.2]octatriene bridgehead system. The first and simplest member of this family, triptycene was obtained by Bartlett et al. [1] in 1942. In the next 40 years, iptycene chemistry had not attracted much attention, and the studies almost focused on the synthesis and reactions of triptycene and its derivatives. In 1981, Hart et al. [2] first proposed the concept "iptycene" based on triptycene, denoting the number of arene planes separated by a bridgehead system. Since then, the door of iptycene chemistry has truly been opened, and the potential applications of iptycenes and their derivatives with unique three-dimensional rigid structures have been gradually developed. In recent years, iptycenes and their derivatives, especially triptycenes [3–10] and pentiptycenes [4, 5, 11, 12] have drawn much attention, and more and more applications in molecular machines, supramolecular chemistry, material science, coordination chemistry, sensor applications, and many other research areas have been discovered. It can be believed that iptycene chemistry is winning more and more chemists' attentions, and walking into its golden age with great opportunities and challenges. In addition, this year also marks the 70th anniversary for the development of iptycene chemistry (1942–2012).

During the 70 years of iptycene chemistry, there were some relevant reviews [3–18]. However, most of the reviews were focused on the limited area(s), and reported in recent several years. Swager [4] reviewed his group's work on synthesis of iptycene-based conjugated polymers and their applications in materials science in 2008. In the same year, Yang and Yan [11] reviewed the synthesis and applications of central-ring functionalized pentiptycenes. In 2009, Chong and MacLachlan [5] briefly described the applications of iptycenes in supramolecular and materials chemistry. Some mini-reviews on the applications of iptycene derivatives in medicine chemistry [14], microporous polymers as potential hydrogen storage materials [16], and physical organic chemistry [6, 17] have also been reported in the past several years. Moreover, a recent feature article on the synthesis of novel triptycene-derived hosts and their applications in molecular recognition and molecular assemblies [8] has been published. More recently, Jiang and Chen [18] also highlighted the synthesis

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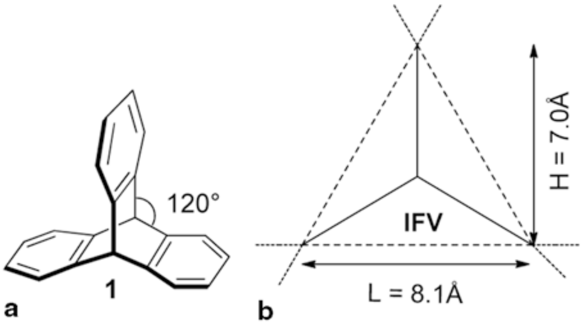


Fig. 1.1 **a** Structure of triptycene **1**. **b** Dimension of **1** with definition of "IFV"

and applications of triptycene and pentiptycene derivatives during last 10 years. In this book, we will discuss in detail not only the synthesis but also the applications of iptycenes and their derivatives. Firstly, we will introduce various methods for the synthesis and functionalization reactions of triptycenes, pentiptycenes, other higher iptycenes, heterotriptycenes, and homotriptycenes, as well as the methods for the preparation of iptycene-based polymers. Then, the applications of iptycenes in different areas will be discussed, according to the different disciplines and molecular behaviors.

1.2 Structure Properties

Triptycene has D_{3h} symmetry with a unique Y-shaped rigid structure (Fig. 1.1a), like "the triptych of antiquity, which was a book with three leaves hinged on a common axis" [1]. In this molecule, the three phenyl ring "panels" are connected with the bridgehead carbons. With dimensions calculated from the centroids of the hydrogen atoms at the extremities, the length of triptycene molecule is 8.1 Å, whereas the height is 7.0 Å (Fig. 1.1b) [19]. The [2.2.2] bridgehead system keeps the angle between aromatic rings at 120°, due to the twisting or deformation caused by high energy barrier. In this rigid three-dimensional molecular structure, this three-bladed geometry can hinder efficient packing; the resulting free volumes in the clefts between the aromatic faces were defined as the "IFV (Fig. 1.1b)" by Long and Swager [20]. In addition, triptycene with three benzene rings contains three open electron-rich cavities with rich reactive positions to provide supramolecular interactions with other molecules. These unique structural features with richer reaction positions make them useful for a wide field of applications with good prospects.

As another most common member of iptycene family, pentiptycene with five phenyl rings has two structural isomers: *para*-pentiptycene and *ortho*-pentiptycene (**2** and **3**, Fig. 1.2). For *para*-pentiptycene, it is in D_{2h} symmetry with an H-shaped structure, whereas *ortho*-pentiptycene has a quite different C_{2v} symmetry. There is a "sterically shielded" central benzene ring and four side ones in *para*-pentiptycene scaffold. These unique structural features with richer reaction positions make them a wide field of applications with good prospects.

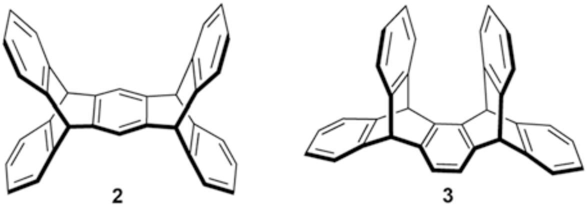


Fig. 1.2 Structures of *para*-pentiptycene **2** and *ortho*-pentiptycene **3**

Compared with triptycene and pentiptycene, the higher iptycenes, like heptiptycene, noniptycene, and nonadecaiptycene, contain more phenyl rings with complicated and diversified rigid structure, along with more than one structural isomers (Table 1.1) [21]. Likewise, the iptycenes with more phenyl rings are in a rigid, nonplanar structure with π-electron-richness character.

1.3 Physical and Chemical Properties

Triptycene is a fine white rhomboid, which is crystallized from methanol–water system. It is very soluble in benzene, soluble in ethyl alcohol, ether, acetone, chloroform, and slightly soluble in methanol. More detailed physical and chemical properties are listed in Table 1.2.

In comparison with triptycene, pentiptycene and the higher iptycene have the poorer solubility in common organic solvent, and face the comparatively difficult situation in synthesis. Thus, comprehensive basic physical–chemical property data are absent.

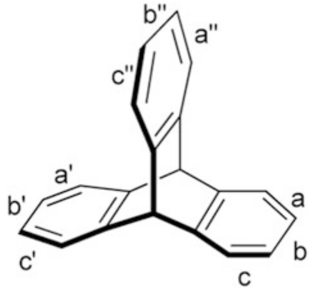
1.4 Spectral Properties

Triptycene is in a unique D_{3h} symmetry rigid conformation, thus its spectral properties exhibit some special characteristics. In the ^{13}C NMR spectrum, there are only four different peaks: 145.27 ppm for C_1, 125.08 ppm for C_2, 123.53 ppm for C_3, and 54.11 ppm for C_4 (Fig. 1.3). The mass spectrum of triptycene exhibits a parent ion at *m/z* 254. There is a group of doubly charged ions spacing at half-mass units between *m/z* 123 and 128 (Fig. 1.4).

There is no recession from aromatic properties in the absorption spectrum of triptycene. It shows a group of strong bands at 211, 264, 271, and 279 nm (Fig. 1.5). It is noteworthy that the near ultraviolet spectrum of triptycene exhibits a differentiable smaller (by a factor of 5) bathochromic shift than that of barrelene [23].

Triptycene can be served as a trimer of three *o*-xylene molecules with a D_{3h} symmetry, covalently bound by methine bridgehead carbons of the type found in

Table 1.1 The possible isomers of iptycenes



Entry	Compounds	Number of isomers	Fusion bonds	Point group
1	Triptycene	1	–	D_{3h}
2	Pentiptycene	2	a	C_{2v}
			b	D_{2h}
3	Heptiptycene	5	ac	D_{3h},
			aa′	C_s
			ab′	C_1
			ac′	C_2
			bb′	C_{2v}
4	Noniptycene	8	aca′	C_1
			acb′	C_s
			aa′a″	C_{3v}
			aa′b″	C_s
			aa′c″	C_s
			ab′b″	C_s
			ab′c″	C_2
			bb′b″	D_{3h}
5	Undecaiptycene	5	aca′c′	C_{2v}
			aca′a″	C_s
			aca′b″	C_1
			aca′c″	C_2
			acb′b″	C_{2v}
6	Tridecaiptycene	2	aca′c′a″	C_s
			aca′c′b″	C_{2v}

Iptycenes derived from triptycene by 9,10-anthradiyl fusions

Table 1.2 Basic properties of triptycene

Empirical formula of triptycene	$C_{20}H_{14}$
CAS Number	477-75-8
Molecular weight (g/mol)	254.3252
Density (g/cm^3)	1.197
Flash point (°C)	171.7
Boiling point (°C)[a]	371.8
Melting point (°C)	252–254

[a] At 760 mmHg

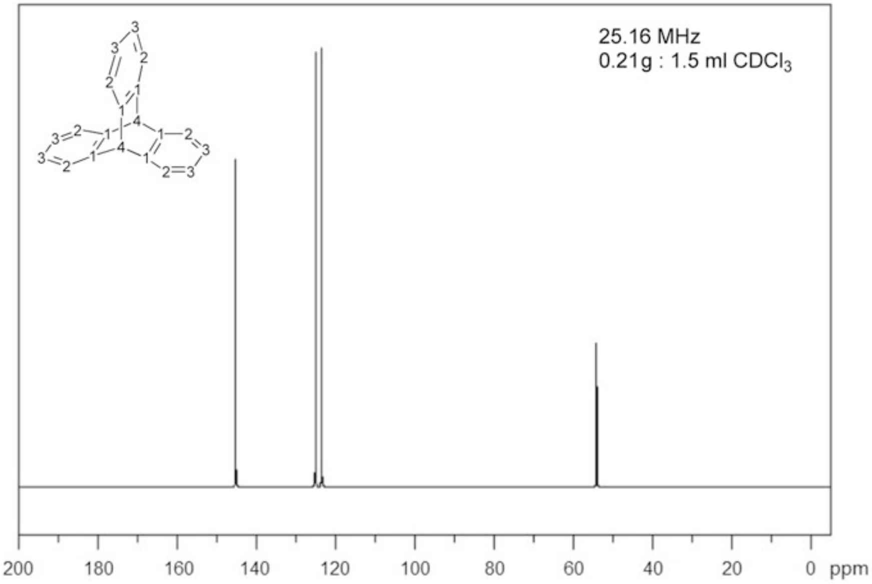


Fig. 1.3 ^{13}C NMR spectrum of triptycene. ([22])

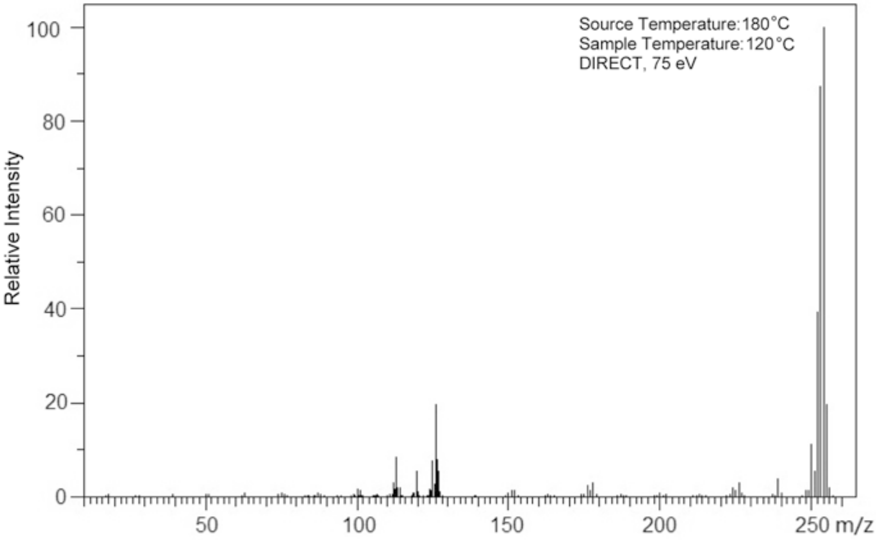
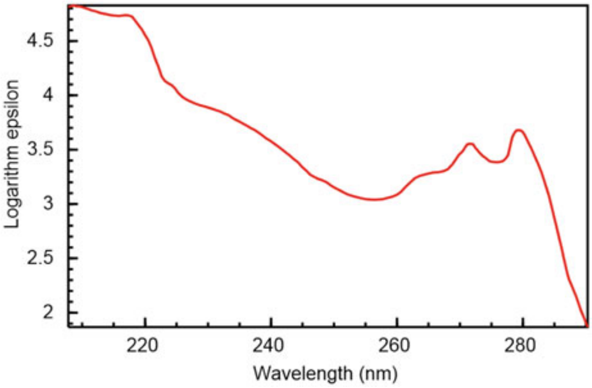


Fig. 1.4 Mass spectrum of triptycene. ([22])

Fig. 1.5 UV/visible spectrum of triptycene. ([24])



[2.2.2]bicyclooctane [25]. It is found that the ground-state vibrational spectrum of triptycene is fit to the low frequency vibrational modes, which is revealed by fluorescence emission, IR, and Raman spectroscopies (Table 1.3).

1.5 Nomenclature

In order to simplify the IUPAC nomenclature, a nomenclature is introduced, which regards triptycene compound as a derivative of dihydroanthracene, and the carbon atoms numbered as shown in Fig. 1.6a or b. However, in some early publications, they numbered the carbon atoms as in Fig. 1.6c, in which triptycene molecules were regarded as substituted bicyclo[2,2,2]octanes. We use the former one in this book.

Table 1.3 Experimental frequencies and intensities of triptycene in the 0–1,000 cm^{-1} range

Entry	Mode	Sym	Frequencies (cm^{-1})			Intensities	
			Raman	IR	LIF	Raman	IR
1	ν_1	e'	62	–	64	0.96	–
2	ν_2	e''	144	–	–	0.35	–
3	ν_3	a_2'	–	–	211		
4	ν_4	e'	354	350	348	0.70	0.11
5	ν_5	a_1'	364	–	–	1.52	–
6	ν_6	e'	478	485	486	0.26	0.55
7	ν_7	e''	495	–	–	0.39	–
8	ν_8	e'	628	626	–	1.00	1.00
9	ν_9	a_1'	648	–	655	0.83	–
10	ν_{10}	a_2''	–	687	–	–	0.02
11	ν_{11}	e'	–	740	748	–	1.51
12	ν_{12}	a_1'	803	–	–	2.22	–
13	ν_{13}	e'	796	797	–	0.91	0.38

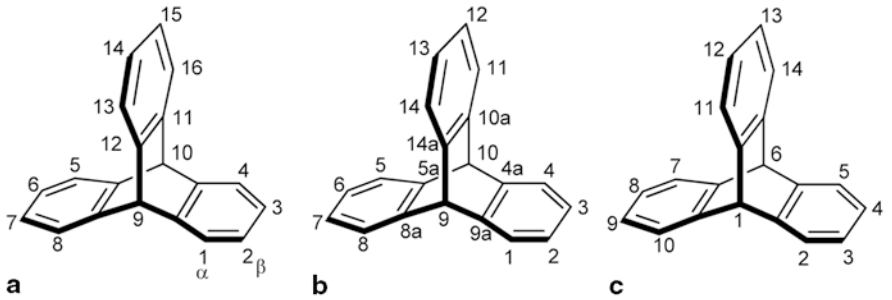


Fig. 1.6 Nomenclature of triptycene

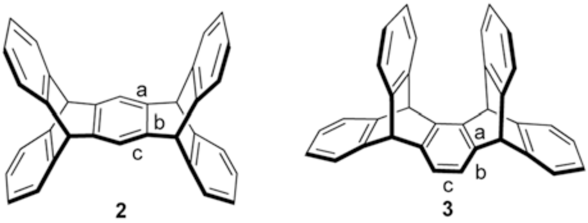


Fig. 1.7 Nomenclature of pentiptycenes **2** and **3**

In 1980s, Hart et al. [2] proposed the concept of "iptycene" originated from the basic unit triptycene. The iptycene molecules are named after the number of arene planes separated by a bridgehead system, for example, triptycene, pentiptycene, and heptiptycene are the system with three, five, and seven phenyl rings, respectively, in which the prefix indicates the number of independent arenes. However, for these larger iptycenes, there is more than one structural isomer. In order to precisely define the structure of iptycenes, Hart et al. had suggested a set of descriptors. The example of pentiptycene illustrates this regulation, both compounds **2** and **3** are pentiptycene, it is named **2** as [1.1.1^b.1.1]pentiptycene and **3** as [1.1.1^a.1.1]pentiptycene (Fig. 1.7), respectively, where "the 1's indicate that each ring is benzenoid and the superscripts (a and b) refer to the bond to which the *sp*^{3} carbons are attached" [11].

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Part II
Synthesis and Reactions of Iptycenes and Their Derivatives

Chapter 2
Synthesis and Reactions of Triptycenes and Their Derivatives

2.1 Synthesis of Triptycenes and Their Derivatives

In order to verify if the triptycyl (the analog of triphenylmethyl in which the three phenyl groups were united to a CH) free radical **1a** (Fig. 2.1) should be more instable than the triphenylmethyl radical itself, Bartlett et al. [1] first synthesized triptycene **1** in a low total yield by a multistep route starting from the Diels–Alder addition reaction of anthracene and benzoquinone (Scheme 2.1) in 1942. Several years later, Bartlett et al. [2] also reported the synthesis of 9-bromotriptycene (**2**) from the 9-bromoanthracene and benzoquinone according to the similar synthetic strategy. However, it was noted that the target compound **2** could be immediately afforded by the deamination of the diamine with $NaNO_2$ in the presence of 50 % H_3PO_2 at −3 °C (Scheme 2.2).

Craig and Wilcox [3] provided a new route to the synthesis of triptycene **1** based on the reduction of triptycene monoquinone, the adduct between anthracene and *p*-benzoquinone, with $LiAlH_4$ or $NaBH_4$. The resulting reduction product was treated with ethanolic hydrochloric acid, and then followed by the chromatography on acid alumina to give the target product **1** in 15 % overall yield.

In 1956, Wittig and Ludwig [4] developed a convenient and one-pot method for the synthesis of triptycene **1** by the addition reaction between benzyne and anthracene. During the next few years, various routes to triptycene via benzyne had been reported. For example, Wittig et al. [4–6] synthesized the triptycene in 30 % yield by the addition reaction between anthracene and organomagnesium reagent generated by the reaction of *o*-bromochloro benzene with magnesium in a THF or ether solution. Soon after, they also reported the synthesis of triptycene **1** by the reaction of chlorobenzene with anthracene in the presence of butyl lithium [7] or $LiSb(C_6H_5)_6$ [8], respectively. Similarly, Sharp and co-workers [9, 10] synthesized triptycene by treating halogenated benzene with potassium *t*-butoxide, followed by the treatment of anthracene [11].

By the addition reaction between tetrafluorobenzyne and anthracene, in 1968, Heaney and co-workers [12, 13] reported the synthesis of tetrahalogenated triptycene **3** in a yield of 42 % (X = F) or 54 % (X = Cl), along with the subsidiary product **4** (Scheme 2.3).

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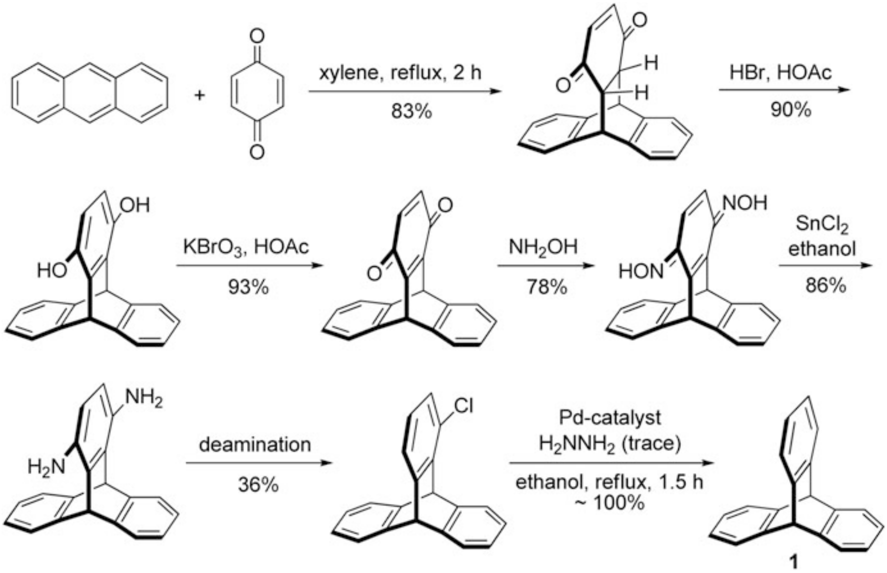
1a

Fig. 2.1 Structure of triptycyl free radical **1a**

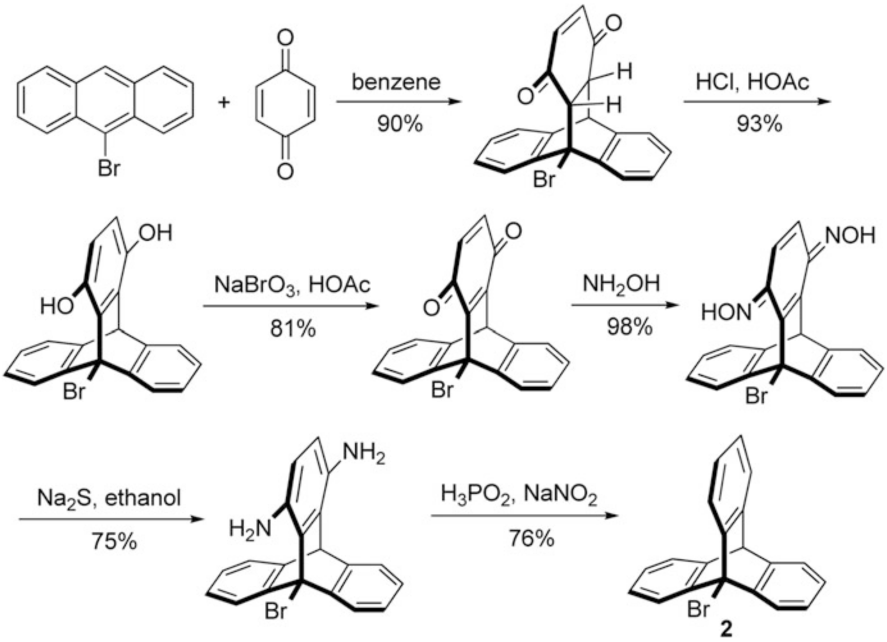
In 1964, Cadogan and Hibbert [14] reported the synthesis of *t*-butyl-substituted triptycene **5** by the reaction of anthracene with the corresponding aryne, which was formed by the heterolytic cleavage of *o*-*t*-butyl-*N*-nitrosoacetanilide in benzene (Scheme 2.4a). Followed by the similar synthetic route, Cadogan and co-workers [15] further synthesized the di-*t*-butyl-substituted triptycene **6** in a 16 % yield by the addition reaction of the corresponding di-*t*-butyl-substituted aryne with anthracene in benzene (Scheme 2.4b).

Depending on the different processes of generating benzyne or arynes, triptycene (Table 2.1) or substituted triptycenes could be obtained in different yields, which might also be regarded as a standard for testing the reactivity of benzyne or arynes.

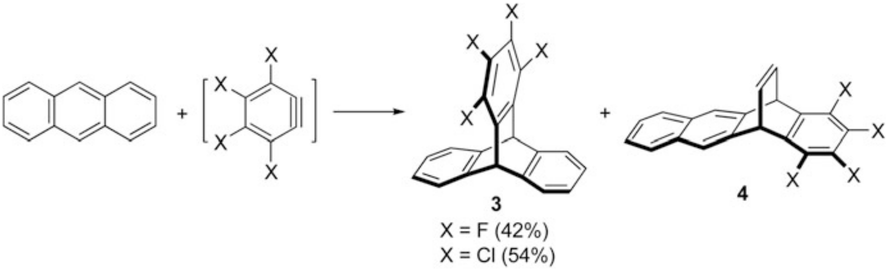
In 1960, Stiles and Miller [21] reported the synthesis of triptycene **1** in 30 % yield by using the *o*-diazonium benzoate as the precursor of benzyne, which provided a more convenient and efficient method for the synthesis of triptycene than the previous ones. Soon after, Friedman and Logullo [25] described another type of precursor for



Scheme 2.1 Synthesis of triptycene **1** from anthracene with benzoquinone



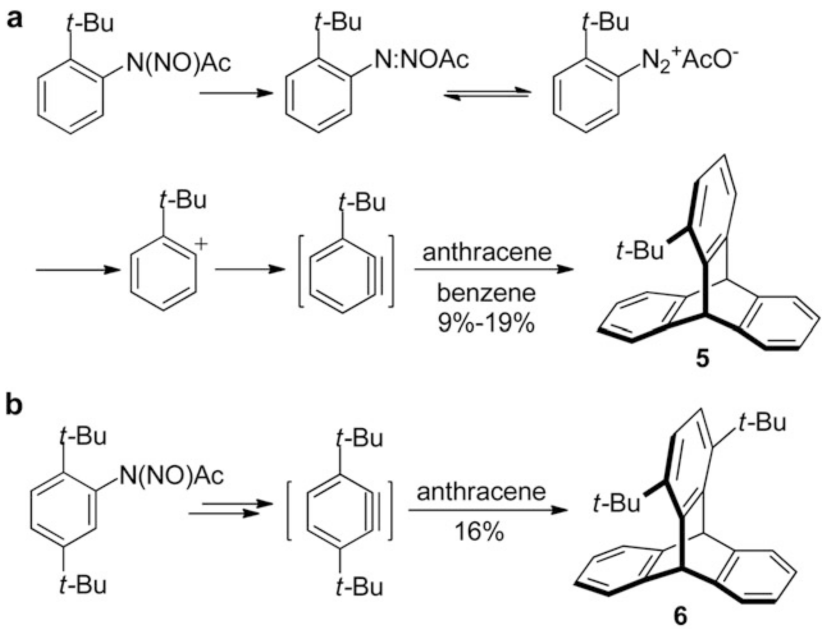
Scheme 2.2 Synthesis of 9-bromotriptycene **2**



Scheme 2.3 Synthesis of tetrahalogenated triptycene **3**

releasing benzyne in situ. As shown in Scheme 2.5, the diazotization of anthranilic acid in nonprotonic solvent in the presence of amyl nitrite could form benzyne in situ; then, the freshly prepared benzyne reacted with anthrancene and gave triptycene in 50–60 % yield. Moreover, the yield could be further improved up to 70–80 % by using a molar excess of anthracene or anthranilic acid.

To generate benzyne with high efficiency under mild conditions, Kitamura et al. [26] described a novel type of hypervalent iodine benzyne precursor. This hypervalent iodine precursor ((phenyl)[[2]-(trimethylsilyl)phenyl]iodo-niumtriflate) reacted with anthracene to afford the Diels–Alder adduct **1** in 86 % yield at room temperature (Scheme 2.6).



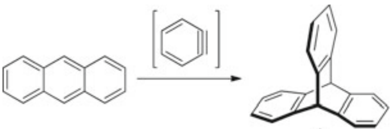
Scheme 2.4 Synthesis of *t*-butyl-substituted triptycene **5** and di-*t*-butyl-substituted triptycene **6**

On the basis of Logullo and Friedman's methodology [25], Kornfeld et al. [27] investigated the reactivity of benzyne toward 9-substituted anthracenes. As shown in Table 2.2, it was found that the different substituents in the anthracene markedly influenced the yields of the triptycene derivatives. According to these results, it was obvious that the yields were relatively high for the anthracenes with electron-donating substituents. By contrast, for the anthracene derivatives with electron-withdrawing groups the yields were unsatisfactory. Particularly, for some strong electron-withdrawing groups (such as R = CHO), there seemed to be no reactions between the 9-substituted anthracenes and benzyne. Although the acetals (Table 2.2, entries 4 and 5) had closed electronic factors, the results were different from their varied steric effect.

Similar to the method developed by Le Goff [24] (Table 2.1, entry 11), Wilcox and Roberts [28] reported the synthesis of diphenyl-substituted triptycene (**7**) in 65 % yield by the reaction between 1,4-diphenylanthracene and benzyne, which was generated in situ from diphenyliodonium-2-carboxylate (Scheme 2.7). According to the procedure of Friedman and Logullo [25], the target compound **7** could be also obtained in 57 % yield with anthranilic acid as a precursor. It was noted that the crude product **7** could be crystallized from the CCl_4 or cyclohexane solution to form complexes, in which the former was more stable.

In 1965, Klanderman [29] investigated the reaction between benzyne and disubstituted anthracenes in detail. As shown in Scheme 2.8, benzyne tended to react in Diels–Alder fashion with the B ring of anthracene **8** to form triptycene **9** or A ring to

Table 2.1 Synthesis of triptycene **1** by the reaction of anthracene with benzyne



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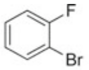
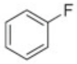
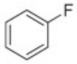
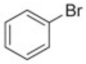
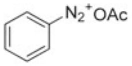
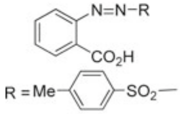
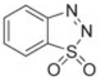
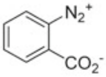
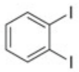
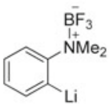
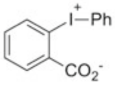
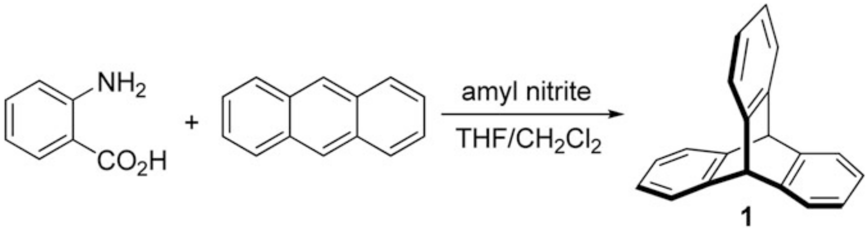
Entry	Precursors	Conditions	Yield (%)
1		Mg, heat	30 [7]
2		BuLi, r.t.	10 [7]
3		$LiSb(C_6H_5)_6$, r.t.	23 [8]
4		*t*-BuOK, reflux	21 [9]
5			10 [16, 17]
6		heat	13 [18]
7			21 [19, 20]
8		heat	30 [21]
9		Zn, 550° C	8 [22]
10		heat	11 [23]
11		heat	23 [24]



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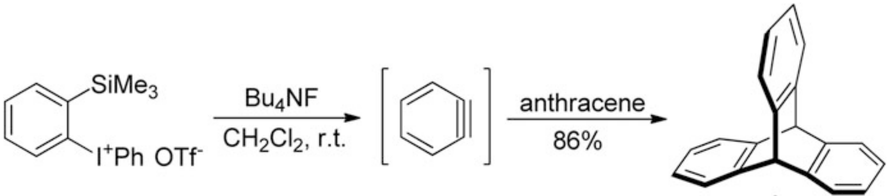
Scheme 2.5 Synthesis of triptycene **1** by using the *o*-diazonium benzoate as the precursor of benzyne



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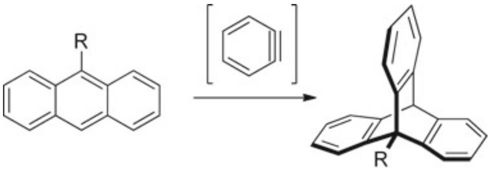
Scheme 2.6 Synthesis of triptycene **1** with hypervalent iodine benzyne precursor

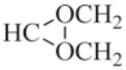
form adduct **10**. The regioselectivity could be controlled by changing the substituents on the anthracene. For the reactions of anthracenes with electron-drawing groups, like cyano group, the ratio of A-ring to B-ring adducts would obviously increase, although, the total yield of the adducts decreased considerably.

Soon after, Klanderman and Criswell [30, 31] also studied the relative reactivity of a number of anthracenes with end-ring substituents toward benzyne. The results showed that benzyne would react in Diels–Alder fashion with all the A, B, and C rings of anthracenes (Scheme 2.9). The characteristics and locations of substituents in the anthracene system greatly influenced the rate of reactions. In general, the electron-donating substituents enhanced the reactivity of the substituted rings to benzyne, whereas the electron-withdrawing substituents lowered it. Furthermore, the steric requirements of benzyne were also considered. However, it was found that except 9,10-diphenyl anthracene, substituents in one ring had no or little effects on the reaction between the other ring and benzyne.

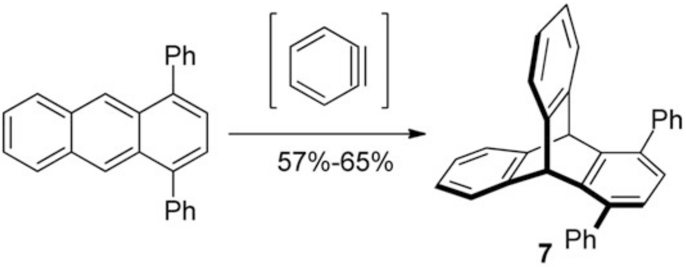
Afterward, Kadosaka and co-workers [32] reported the synthesis of a series of chloro substituted triptycenes by the treatment of benzyne or chlorobenzyne with various chloroanthracene. The mono chlorotriptycene (**15**, Scheme 2.10), dichlorotriptycenes (**16**, **17**, Scheme 2.11) and trichlorotriptycenes (**18**, **19**, Scheme 2.12) could be obtained via the corresponding Diels–Alder reaction of benzyne with chloroanthracene, or chlorobenzyne with anthracene, followed by the Logullo and Friedman's procedure [25].

Table 2.2 Triptycenes prepared from 9-substituted anthracenes



Entry	R	Yield (%)
1	NO_2	15
2	CH_2Cl	70
3	CH_2OH	6
4	$CH(OCH_3)_2$	4
5	 $HC{<}^{OCH_2}_{OCH_2}$	53
6	CHO	-
7	CH_2CH_2Cl	49
8	$CH_2CH_2CO_2CH_3$	50

Particularly, the addition of 3-chlorobenzyne to the 9-substituted anthracene would give a mixture of two isomers: quasi-*cis*- and quasi-*trans*-isomer (**20**, Scheme 2.13). In this case, it was believed that the inductive effect of the substituents would take the leading role in determining the ratios of the isomers, whereas the steric effects had almost no or little contributions.



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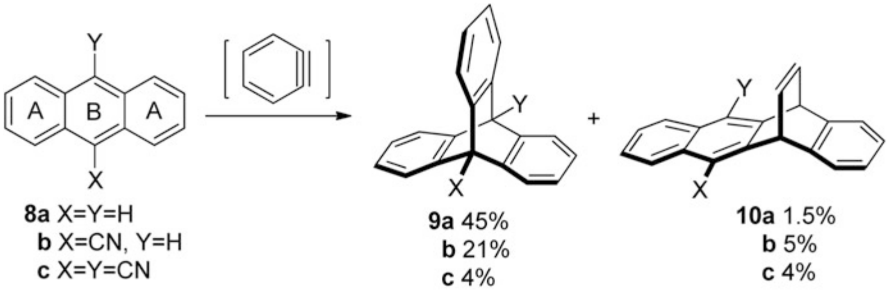
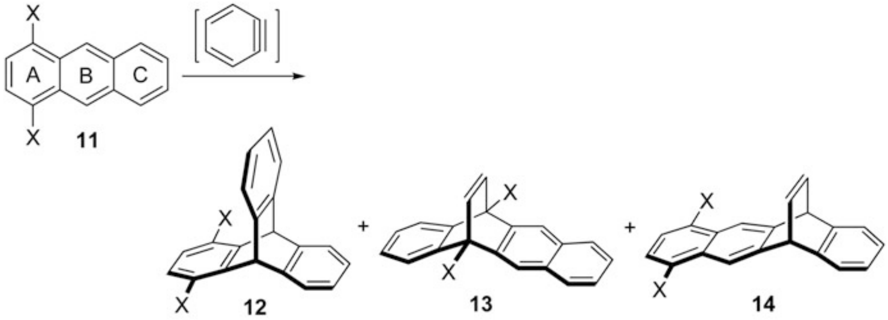
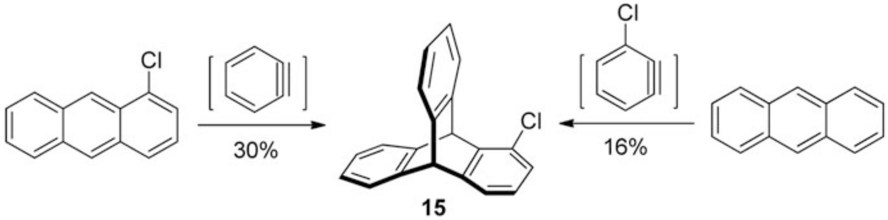
Scheme 2.7 Synthesis of compound **7**



Scheme 2.8 Reaction between benzyne and disubstituted anthracenes **8**



Scheme 2.9 Reaction between benzyne and anthracenes **9** with end-ring substituents



Scheme 2.10 Synthesis of monochlorotriptycene **15**

Subsequently, Rogers and Averill [33] synthesized a series of 1,8,13- and 1,8,16-trisubstituted triptycenes by the treatment of 1,8-disubstituted anthracenes with monosubstituted benzynes, based on Kadosaka's synthetic strategy [32]. As shown in Table 2.3, the nature of the substituents on the anthracene and benzyne units had obviously influenced the ratio of *syn/anti* isomers. However, it was further found that this stereo selectivity mainly depended on the substituents of benzynes.

Following the route of Friedman and Logullo [25], Klanderman and Faber [34] reported the synthesis of 9,10-bis(acetoxymethyl)triptycene (**21**) from 9,10-bis(acetoxymethyl)anthracene, which was generated by the reaction of 9,10-bis(chloromethyl)anthracene with potassium acetate and acetic acid (Scheme 2.14a).