Summary of

The Thesis Entitled

Studies in the synthesis and chemistry of aesthetically pleasing carbocyclic compounds

Submitted to

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

By

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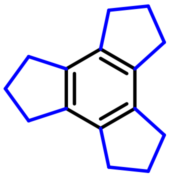
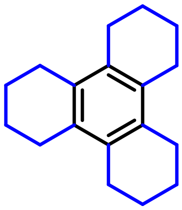
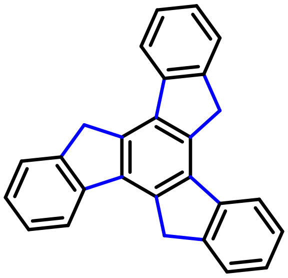
DECEMBER-2022

Benzocyclotrimers (BCT) are symmetrical trisannelated benzene derivatives derived from cyclotrimerization of corresponding ketones.[1] BCTs such as trindane **1**, dodecahydrotriphenylene **2** and truxene **3** have recently received much attention due to their potential in constructing higher polyhedra which can have diverse applications in semiconductors, liquid crystalline materials, and organic photovoltaic cells amongst many others.[2] Compounds **1,** **2** and **3** can be easily synthesized *via* acid-catalyzed cyclocondensation of cyclopentanone, cyclohexanone and indanone respectively.[3]


Trindane **1**


Dodecahydrotriphenylene **2**


Truxene **3**

The **first chapter** of the thesis provides introduction about the methodology for the preparation and reaction of various BCTs, which are potential precursors for complex molecular architectures. Small molecules as a building block of rigid or moderately flexible supramolecular framework, can serve as scaffold to construct fullerenes, graphenes and many other polyhedra. (**Figure 1**)

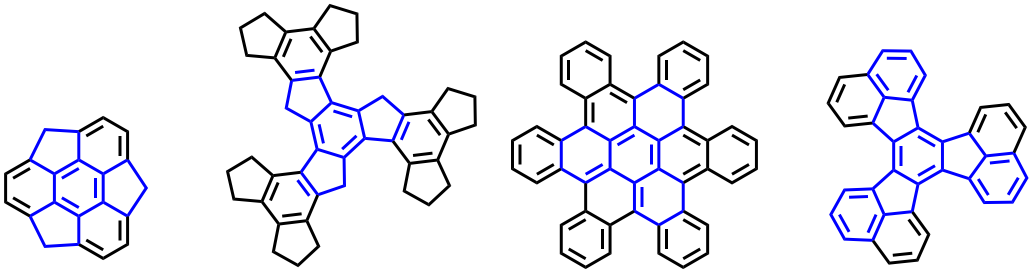

Sumanene Trimer of trindanone Hexabenzocoronene Decacyclene

Figure 1. Symmetrical polyarenes having BCT scaffold

Selective benzylic oxo-functionalization is an important protocol towards the construction of polyarenes.[4] BCT fragments are presents in buckminsterfullerene, graphene and other higher polyhedra.[5] (**Figure 2**)

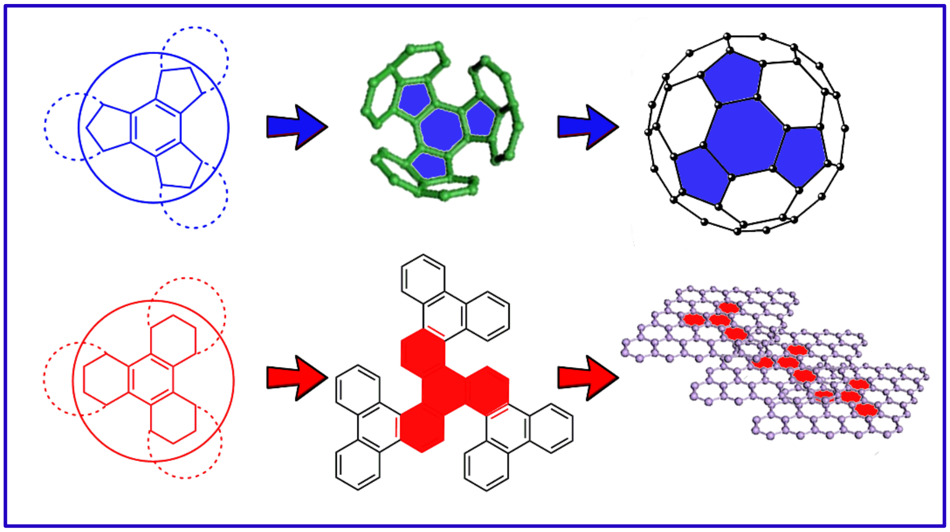
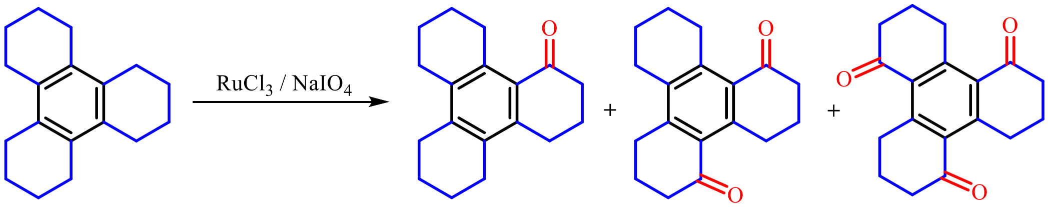


Figure 2. BCTs present in fullerene and graphene

The **second chapter** of the thesis describes chemistry of ruthenium catalyzed oxidation of dodecahydrotriphenylene **2**. Ruthenium complexes are believed to be highly potential oxidizing agents which vigorously attack sp^2 C-H sites of the molecules. Controlling selectivity in Ru-catalyzed oxidation is a big challenge due to the involvement of various high-valent ruthenium species during the course of oxidation. Hence, complexes using various ligands with ruthenium have been employed to achieve selective benzylic sp^3 C-H oxidations.[6] Interestingly, the oxidation of trindane **1** has been shown to yield a highly functionalized ring-opened product upon oxidation with ruthenium.[3a]

In context with our synthetic studies, we became interested in examining similar oxidation of dodecahydrotriphenylene **2** using $RuCl_3$–$NaIO_4$ system.



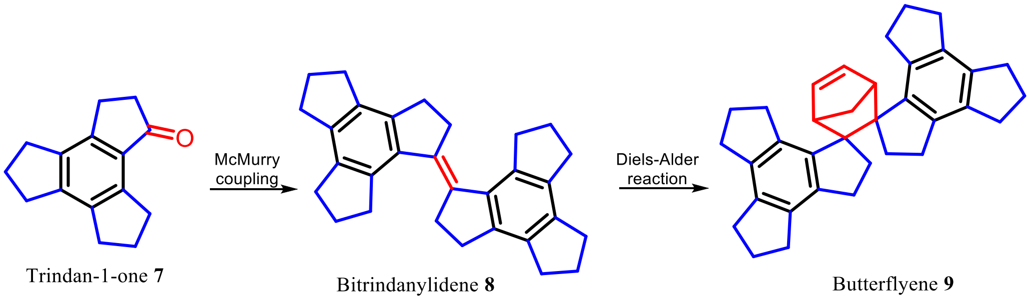
2 4 5 6

Scheme 1. Ruthenium mediated oxidation of dodecahydrotriphenylene **2**

The reaction of **2** with ruthenium trichloride–sodium periodate furnished **4**, **5** and **6**. We have also undertaken a time dependent study to examine the behavior of compound **2**. (**Scheme 1**) It is indeed surprising to note that the above reaction furnished mono, di- and tri-keto derivatives in which the aromatic ring remains intact during ruthenium catalyzed oxidation. This is in stark contrast to the observation that the trindane **1** undergoes complete oxidative cleavage of the aromatic ring.[3a] Density functional theory (DFT) calculations have also been carried out which reflect close agreement with experimental findings.[7]

The synthesis of molecular architectures with strained and sterically hindered characteristics is a difficult task for synthetic chemists. Such molecules may possess unique characteristics such as chirality, supramolecular assembly, optical and electronic properties.[8] Especially, geodesic polyarenes with complex architectures and fascinating geometries have been reported in the literature.[9]

The **third chapter** describes a short and expedient synthetic protocol towards quick acquisition of an attractive polycyclic skeleton resembling to the shape of a butterfly in four simple steps from cyclopentanone. This prototype decacyclic ring system has been synthesized *via* cyclocondensation, benzylic oxidation, McMurry coupling, and Diels−Alder reaction successively. (**Scheme 2**)



Scheme 2. Synthesis of butterflyene **9**

Trindanone **7** *via* McMurry coupling resulted in the formation of bitrindanylidine **8**. The ***trans*** geometry in **8** was confirmed through the Single-crystal X-ray diffraction studies.

The intriguing chemistry of carbonyl compounds has attracted significant synthetic interest as it can produce new functionalities and it can also lead to new C-C bond formation.[10] Functionalization of the peripheral ring systems in trindane and dodecahydrotriphenylene has been explored and discussed in the **fourth chapter**.

In conclusion, we have developed facile and expedient strategies for the synthesis of functionalized carbocycles using trindane and dodecahydrotriphenylene.

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