QUEST FOR 'BUCKY-BALLS' AND 'BUCKY-BOWLS': AN ODYSSEY THROUGH THE SCIENCE OF ORGANIC SYNTHESIS*

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Fullerene era has come to stay. Their discovery has generated enormous interest not only in their potentially rich chemistry but also in their fragments, the 'bucky-bowls'. Access to fullerenes (bucky-balls) and bucky-bowls through classical approaches constitutes a formidable synthetic challenge. Many synthetic chemists around the world, have been enticed into this arena. We too have launched an initiative in this direction and several new and conceptually simple approaches to fullerene fragments (bucky-bowls), that can be eventually amplified to fullerenes (bucky-balls) have been conceived and explored. Particularly noteworthy has been the exceptionally short synthesis of C_{27}-symmetry, C_{50}-corannulene from readily available, bench-top starting materials. Firm foundation for the synthesis of C_{21}-sumanene, representing a dominant feature on the C_{60} surface along C_{3} symmetry pathway, has been laid. In this context, a synthesis of seco-sumanene has been accomplished. A three-step synthetic sequence consisting of a Wittig olefination, oxidative photocyclization and flash vacuum pyrolysis (FVP) has been devised to access higher order bucky-bowls. This approach has been explored towards the short synthesis of C_{30} and C_{48}-fragments of C_{60}. Exceptionally short synthesis of C_{37}-hemifullerene and C_{47}-hemifullerene have been accomplished. The former hemifullerene represents the exactly half of C_{60} and in principle can be dimerized into it. Approaches to C_{32} and C_{48} have been explored. Efforts of other groups in this area have also been summarized. Our accomplishments in this area, to date, compare very well with those of other groups around the world.

Key Words: Fullerenes; Wittig Reaction; Photocyclization; Pyrolysis

Introduction

Fullerene is a generic name (coined after the American architect R Buckminster Fuller who built the legendary Geodesic Dome for the US exhibit at the EXPO’67 in Montreal) bestowed on a new form of molecular carbon consisting of stable cage-like structures of diverse shape, size and symmetry. It is built-up of hexagons and pentagons; with the latter rings interspersed within the graphitic polycyclic aromatic hydrocarbon sheets providing the necessary curvature to eventuate into spherical architecture. The building principle of fullerenes, C\_n (n>20), is based on Euler’s theorem which predicts that twelve pentagons are needed for the complete closure of each spherical hollow net composed of (C\_n-20)/2 hexagonal rings. The stability of the resulting fullerene cage structure may be explained on the basis of the isolated pentagon rule (IPR), which predicts that cyclic cages with isolated pentagons are more stable than those having adjacent pentagons. While an unlimited range of fullerenes varying from C\_28 'bucky-baby' to C\_340 'giant bucky' (Scheme 1A) and beyond are conceivable, only a few of them have been prepared and characterized so far. Among them, C\_60, the buckminsterfullerene, is pre-eminent by virtue of its stability, abundance and truncated icosahedral symmetry (\textit{Ih}). Its shape is unique in all of chemistry.
There are thirty-two rings: 20 six-membered and 12 five membered. Each atom in C_{60} occupies an exactly equivalent site and each is connected in an exactly equivalent way to its neighbours. The chemical bonds between these atoms follow the pattern of the seams on a soccer ball. Not surprisingly, 3 is fondly referred to as the "roundest molecule" and "footballene" etc. A close second among this exotic family of carbon cages is C_{70}, the ellsiodal fullerene 4 of D_{5h} symmetry made up of 12 pentagonal and 25 hexagonal rings with 70 vertices and 37 faces. (Scheme 1B).

While diamond and graphite, the two allotropic forms of carbon are known for a long time and their structures adorn every introductory textbook in chemistry, fullerenes, the latest entrant into the carbon family have a short history. In the early 60's, formation of cyclic cages through the folding of graphite-like sheets was conjectured but such propositions largely remained in the realm of fanciful ideas and their realization did not receive serious attention. Fullerenes, particularly C_{60}, as a distinct structural entity of chemical interest was first conceptualized by Osawa in 1970, as a possible three dimensional super aromatic structure and it was soon subjected to theoretical scrutiny in Japan and Soviet Union. However, the relative obscurity of the journals in which these works were published and the skepticism about the existence of such structures combined to relegate this seminal proposition into the back burners of the world of chemical enquiry. In the early 1980's, Chapman in the US was the only one to pick-up the challenge and muster enough courage to venture into a synthesis of the then unknown C_{60}, albeit unsuccessfully. A breakthrough in the discovery of this new family of carbon cages (fullerenes) came through interest in the understanding of some extraterrestrial events like the conditions under which carbon nucleates in the atmosphere of red giant stars. In this context, refractory carbon clusters, generated in a plasma by focusing a pulsed laser on graphite were subjected to mass spectrometric studies and under a specific set of conditions persistent presence of an unusually intense peak at 720 amu was noticed. In a remarkable confluence of highly skilled experimental observations and intuition, three research groups, working across the Atlantic, drew an epoch making conclusion and attributed this mass peak to an spherical entity bearing the structure of a truncated icosahedron with I_{h} symmetry.12,16 This was 1985 and for this remarkable prescience, the trio of Kroto, Smalley, and Curl were awarded the Nobel prize in chemistry for the year 1996. After five years (1985-90) of dormancy, another breakthrough really announced the arrival of fullerenes on the chemistry scene. In 1990 Kratschmer and Huffman, with the intent of producing analogues of interstellar dust by vaporization of graphite rods reported the formation of a soot that could be sublimed or extracted with benzene to give macroscopic quantities of fullerenes rich in C_{60}. This not only made it possible to fully characterize C_{60} through conventional spectroscopic methods (UV, IR, ^{13}C NMR, etc.) but generated a world-wide race to obtain it in preparatively useful yields. Many experimental innovations and separation regimes were quickly developed and by 1992 bench-top fullerene generators were in vogue and C_{60} became a commercial product available in gram quantities at an affordable price. Further explorations of the graphite derived soot and residues has revealed besides the spherical cages, tube like structures of several nanometer length with closed tips, called bucky-tubes or nanotubes and carbon onions with single or multiple shells. Thus, a unique new microworld made up of interconnecting carbon domes and tubes has emerged with tremendous possibilities in the development of nanotechnology.

The ready accessibility of C_{60} resulted in a world-wide 'treasure hunt' to unravel its potentially rich and varied reactivity pattern. Indeed, a myriad reagents and every possible organic reaction-type ranging from nucleophilic and radical additions to diverse cycloadditions were tried with C_{60} and this fascinating molecule did not disappoint the explorers. While the anticipated 'super aromatic' character was not displayed by C_{60}, it did exhibit
weakly aromatic traits together with propensity to undergo reduction by accepting up to six electrons and engaged partners in cycloadditions by functioning as a $2\pi$ component. Indeed, an unprecedented number of fullerene derivatives have been prepared and subjected to scrutiny for various properties. Thus, dimers, copolymers and dendrimers, hybrids with sugars, calixarenes, amino acids and porphyrins amongst others, and exo- and endo-hedral complexes with various metals have been prepared. Properties ranging from superconductor to insulator, from diamond to teflon($C_{60}$-$F_{60}$?) and even anti-cancer to anti-AIDS have been observed or prophesized for the $C_{60}$ derived entities. In short, while fullerens and their derivatives hold great promise as new materials and therapeutic agents of future, their immense potential has not been realized so far. Concerns about their toxicity also remain to be fully addressed.

As the fullerene band wagon rolled on full steam and many facets of their exciting chemistry unfolded, those reveling in the art of organic synthesis found it embarrassing and disconcerting that a beautiful molecule of such complexity and high symmetry like $C_{60}$ was prepared by 'arching' graphite or by the extraction of soot produced by burning aromatic $\beta$ hydrocarbons. While these preparations of $C_{60}$ were reminiscent of alchemy or 'black-box' operations, yet they emboldened some to suggest that if molecules of the complexity of fullerens can be made so effortlessly (and thoughtlessly!), synthetic chemists are hardly needed. Synthetic organic chemists around the world, although scornful of such forebodings, nonetheless picked up the gauntlet and several groups around the world ventured to undertake an odyssey towards the synthetic conquest of $C_{60}$.

The pursuit of buckminsterfullerene($C_{60}$) through classical synthetic protocols constitutes a formidable intellectual and experimental challenge and for the moment remains a somewhat distant objective for the synthetic chemist. However, there are clear prospects of many interesting findings along the way in such endeavours as the different segments of $C_{60}$ are targeted and the curved surface of fullerens begins to evolve. Familiar, planar aromatic species like benzene, naphthalene, phenanthrene and pyracylene can be readily recognized on the fullerene surface. But, when one ventures to identify segments composed of more than twenty carbon atoms with imbibed pentagon rings, on $C_{60}$, a range of non-planar, polycyclic aromatic species of different shape and symmetry begin to emerge. On adding hydrogens to the end carbons of these entities to satisfy the valency, a novel class of non-planar polycyclic aromatic hydrocarbons (PAHs) can be generated and they are now commonly referred to as 'bucky-bowls' because of their bowl-like shape. The 'bucky-bowls', as non-planar PAHs are expected to exhibit physico-chemical properties quite different from their planar analogs. For example, the curvature gives them the choice to complex metal ions either from endohedral (concave) or exohedral (convex) face. It may be of interest also to find out the required bowl-depth in these non-planar PAHs for displaying fullerene like activity. However, 'bucky-bowls' are not produced along with fullerens (bucky-balls) during the graphite arcing process and therefore can only be accessed through directed synthetic endeavours. Thus, devising strategies towards 'bucky-bowls' itself constitutes a major synthetic enterprise.

Synthetic efforts towards $C_{60}$ along classical lines is not an ordinary venture and can be a very demanding proposition in terms of planning, experimental skills, resources and patience, and yet this molecule has enticed many researchers around the world and our group at the University of Hyderabad was among the first few to enter the arena in pursuit of $C_{60}$. In this account, we provide an overview of our travails, which includes evolution of our synthetic strategies, our many successes and some failures. While the focus here is mainly on our own efforts, contributions of others wherever relevant have been duly referred to.

Retrosynthetic Analysis

To delineate possible synthetic routes to $C_{60}$ and its 'bucky-bowl' precursors, its complex polycyclic framework has to be subjected to a systematic retrosynthetic analysis. This exercise can be carried out in a myriad different ways. However, keeping in mind the high symmetry ($I_h$) of $C_{60}$, we sought to initially limit the retrosynthetic analysis along $C_7$, $C_7$, and $C_5$-symmetry pathways to logically partition the carbon sphere. (Scheme 1). This simple exercise enabled the identification of a
relatively small number of curved surfaces 5-16 from the formidable 3\textsuperscript{49-51}. Attachment of hydrogens to end-carbons of 5-16 to satisfy the valence requirements leads to the generation of synthetically realizable non-planar PAHs. Among them, corannulene 16, C\textsubscript{20}H\textsubscript{10}, and sumanene 12, C\textsubscript{21}H\textsubscript{12}, appeared to be the

`simpler and most readily identifiable motifs on the fullerene surface. Indeed, both 12 and 16 represent the polar caps (the Arctic and the Antarctic zones!) of C\textsubscript{60} and their separation from the mother sphere as shown in the Schemes 2 & 3, not only identifies them as possible advanced building-blocks for the synthesis of fullerenes but also provides important clues about how the pieces can be put together. Corannulene 16 and sumanene 12 can be regarded as the first generation ‘bucky-bowls’ which possess pronounced curvature and bowl-depth and their structural and bonding parameters resemble those of C\textsubscript{60}. Their syntheses obviously constitute a major stepping stone towards the ultimate conquest of C\textsubscript{60} and have garnered much attention in recent years.\textsuperscript{42-45} Looking further ahead, the retrosynthetic theme depicted in Scheme 1 also identifies some advanced precursors 7, 11 and 15, containing half the carbon content of C\textsubscript{60}, as the second generation ‘bucky-bowls’ in which fullerene characteristics should begin to manifest. Among these C\textsubscript{30}-hemifullerenes 7, 11 and 15, the C\textsubscript{3}-symmetry sibling 11 (triindenotriphenylene) is particularly noteworthy in being the exact half of C\textsubscript{60}, which can in principle dimerize (\textit{vide infra}) to close the fullerene sphere Scheme 2 & 3. Not unexpectedly, hemifullerenes 7, 11 and 15 have elicited considerable response from the synthetic chemists. In Scheme 1, another set of deep ‘bowls’ 5, 6, 9, 10, 13, 14 have been identified as possible targets en route to C\textsubscript{60}, but efforts towards them, if any, are still on synthetic chemists drawing boards.

Having identified the key building blocks for C\textsubscript{60} in the form of ‘bucky-bowls’ 12 and 16, it was time to consider the strategic options towards their creation. After some thought and careful weighing of various possibilities, we decided to pursue an approach that in some sense resembled the formation of fullerenes from graphite. It was reasoned that appropriately designed polycyclic aromatic hydrocarbons under thermal activation, like FVP (flash vacuum pyrolysis), could ‘curl-up’ through transannular C-C connection. The FVP regime facilitates such peri-bridging by making available the required high energy conformations.
of PAHs which are otherwise not accessible. Under the FVP conditions, the aromatic nuclei of PAHs not only deform but also generate reactive intermediates like benzynes, carbenes, aryl radicals etc., which undergo insertion reactions into the nearest peri C-H bonds. \(^{52-64}\) A seminal example of this is by Brown et al. who have shown that terminal alkyne 17 rearranges to isomeric vinyl carbone intermediate 18 under FVP which then inserts into the nearby peri-C-H bond to furnish the cyclopentannulated product 19, (Scheme 4). Several examples of similar peri-C-C connectivity in PAHs during FVP has been reported and invariably lead to a curvature generating five-membered ring formation. Such cyclizations are facilitated by the introduction of a halogen substituent into one of the fjord regions of the PAHs (20 \(\rightarrow\) 21 and 22\(\rightarrow\)23), Scheme 5. On the basis of these examples, one can readily surmise that FVP is destined to play a pivotal role in the synthetic quest for fullerenes.\(^ {57-69}\)

**Scheme 4**

\[ X = Y = F, 1150 ^\circ C, 32\%; X = Cl, Y = H, 1030 ^\circ C, 53\%; X = I, Y = Cl, 950 ^\circ C, 75\%. \]

**Scheme 5**

With the identification of FVP as the key ultimate step in the synthesis of ‘bucky bowls’ and ‘bucky ball’, the remaining main concern was the assembly of the precursor PAHs. For this purpose, Wittig olefination between appropriate partners to give stilbene-like intermediates and oxidative photocyclization of the resulting products to the condensed polycyclic aromatics appeared to be an exceptionally short and viable strategy. A generalized version of our short approach in which Wittig olefination (24 +25\(\rightarrow\)26) and

**Scheme 6**
photocyclization (26→27) have been integrated with the FVP (27→28) step is depicted in Scheme 6. It is implicit in this approach that symmetry considerations should receive adequate attention and depending on the symmetry of the target, many-fold Wittig reactions and photocyclizations could be contemplated on a single substrate.

Concurrently with the evaluation of synthetic aspects, we have also carried out complementary study of the detailed molecular structure of 5-16 and other related C₆₀ fragments using MM2 and MNDO calculations.49-51 The bond length, bond angles, bond-fixation and bond-depth parameters in 5-16 have been incisively analyzed and compared with C₆₀ to establish their kinship. The ‘bowl-to-bowl’ inversion barriers in these ‘bucky-bowls’ have also been calculated and in the case of corannulene 16, they are in good agreement with the experimental results. More importantly, the calculations enabled a critical assessment of the strain build-up in bucky-bowls, 5-16 as they evolve towards C₆₀. This proved invaluable in the appraisal of various synthetic strategies and in the choice of the final route in almost all the cases.

On the strength of the logical analysis and computational results eluded above, we felt confident enough to launch our synthetic efforts towards ‘bucky-bowls’ and planned to eventually take on the ‘bucky-ball’ itself. For the sake of convenience, the results are best presented in terms of the specific targets that we pursued and which were identified through the retrosynthetic theme depicted in Scheme 1.

**Corannulene 16 And Its Analogs**

The bowl shaped C₂₀H₁₀ hydrocarbon, corannulene 16, having a central pentagonal ring surrounded by five hexagonal aromatic rings, is a fascinating molecular entity.70-82 It was the main inspiration behind Osawa’s proposed structure of C₆₀ as a super aromatic moiety. The first synthesis of 16 was accomplished over thirty years ago by Barth and Lawton70,71 starting from 3-carbomethoxy-4H-cyclopenta[def]phenanthrene 29 via 30, employing classical ring annulations and functional group transformations, in 17 steps, (Scheme 7). After a period of relative dormancy lasting quarter of a century, interest in corannulene was revived with the advent of the 90’s and the discovery of C₆₀. Several syntheses of 16 have appeared recently72-82 and most of these (A-F→16) are tactical variations of Scott’s pioneering strategy81 involving flash vacuum pyrolysis (FVP) of 7,10-disubstituted-fluoranthene derivatives, (Scheme 8), which in turn were made from 7,10-diacetyl-fluoranthene (31→32→33), (Scheme 9).

Zimmermann et al.82 on the other hand have employed FVP on a bis(trimethylsilyl) derivative of cyclopenta[def]phenanthrene system (G) to access 16. In these FVP mediated syntheses of corannulene, terminal acetylene, halo-vinylidene or trimethylsilylvinylidene functionalities rearrange to the more reactive vinyl carbene intermediates which insert into the nearest peri-C-H bonds and thereby adding two six membered aromatic rings to complete the rim of the curved surface of corannulene.

In our scheme of corannulene synthesis, commercially available 2-methyl naphthalene and p-tolualdehyde were elaborated to functionalized benzo[c]phenanthrene derivative 40 through Wittig reaction, (35+36→37) photocyclization (37→38) and NBS reaction and oxidation (Scheme 10). The formyl derivative 40, obtained from 39 through routine transformations and further elaborated to 41-44, which served as the key precursors for the final step, (Scheme 11). On FVP, each of the precursors 41-44 underwent tandem cyclization and furnished 16 which could be isolated through careful column chromatography on silica gel. Best yield of corannulene 16 (8%) could be obtained from vinyl chloride derivatives 42 and 43. Under FVP conditions, these precursors undergo Ar-Ar coupling to form the five-membered ring and also generate highly reactive vinyl carbene intermediates which insert into the nearest peri-C-H bonds to form one pentagonal and one hexagonal rings. Thus, hexacyclic corannulene could be obtained through a short, straightforward sequence employing simple starting materials and essentially following the tactic conceptualized in Scheme 6.
Structurally embellished derivatives of corannulene with additional annulation or a cyclophane motif have drawn attention because in such systems the extent of pyramidalization and bowl-to-bowl inversion barriers can be controlled and incisively probed.\textsuperscript{54-59} Rabideau \textit{et al.} were the first to report the synthesis of cyclopentannulated derivatives 49 and 50 of corannulene 16 \textit{via} FVP of bischlorovinyl derivative 48, (Scheme 12).\textsuperscript{85} The compound 48 was derived from bis-acetyl derivative 47, obtained from condensation reaction between 1,2-dioxopyracene, 46 and 2,4,6-heptane trione 45. Later, Scott \textit{et al.} reported direct annulation of 16 through Friedel-Craft's acylation and elaboration of the acetylcorannulene to chlorovinyl derivative 51. FVP on 51 delivered 49 (Scheme 12).\textsuperscript{54}

Siegel and coworkers\textsuperscript{76} have conceptualized corannulene based cyclophane motifs, in which 2,5-positions on the corannulene nucleus are attached to \textit{para}-positions of a benzene ring \textit{via} bis(mercaptomethyl)bridges. 2,7-Dimethylace-naphthenequinone 52 was employed as the starting material and following Scott's strategy was elaborated to 2,5-dimethylcorannulene 54 through 53. On benzyl bromination 54 furnished bis(bromomethyl) derivative 55 which on displacement reaction with 1,4-bis(mercapto-
methyl]benzene led to the corannulene based cyclophane 56. Variable temperature NMR studies indicated a single locked conformation for 56 without any 'bowl to bowl' inversion. (Scheme 13).

**Sumanene 12**

As enumerated above, retrosynthetic analysis along the C$_3$-symmetry route led to the identification of a heptacyclic, C$_{21}$H$_{12}$ fragment, 12 which we have named as sumanene (derived from suman, meaning flower in Hindi and Sanskrit) as a prominent motif on the fullerene surface.$^{49,50,93-99}$ The unique structure of 12 is composed of a central six membered ring surrounded by alternate five- and six-membered rings. Presence of two additional pentagonal rings in 12 compared to corannulene imparts greater curvature to the molecule (bowl-depth 1.15 Å compared to 0.87 Å in corannulene).$^{49,50}$ We were the first to recognize the importance of 12, both as a 'bucky bowl' as well as a building-block for C$_{60}$ and initiated synthetic efforts towards it.

Our approach$^{93}$ to 12 was conceptualized in terms of a retro-synthetic analysis depicted in Scheme 14. Thus, C$_3$-symmetry trimethyltriphenylene 57 emerged as our advanced intermediate and commercially available mesitylene 58 as the starting material. A short, practical and flexible route to 12 from mesitylene was developed as summarized in

![Scheme 14](image)

Scheme 15. The key reaction in this scheme was the three-fold Cu(I) catalyzed cross-coupling reaction between tribromide 59 and butenyl magnesium bromide to furnish 60, which on exposure to Lewis acids cyclized to 61. On dehydrogenation, 61 furnished the desired C$_3$-trimethyltriphenylene 57. With access to 57 secured, considerable effort was directed towards establishing the three methano bridges through the transannular insertion of the methyl groups. When 57 was subjected to Pd/C dehydrogenation or flash vacuum pyrolysis only the mono-bridged product 62 was realized, (Scheme 15). Many trials employing different temperature regimes and catalysts proved unsuccessful. Consequently, it was decided to activate the methyl groups in 57 to promote the formation of reactive intermediates for transannular cyclization. Towards this objective, 57 was transformed to tris-bromomethyl-triphenylene 63 and subjected to FVP. The major product was the dimethano-bridged compound 64. There were some indications, based on the $^1$H NMR data that minute amounts of sumanene 12 might be lurking in the pyrolysate from tribromide 63. However, purification and definitive characterization of 12 has not been possible so far. It is also not inconceivable that 12, if formed, reverts back to 62 or 64, during FVP conditions. Nonetheless, we consider the attainment of the doubly-bridged compound 64, a substantial stepping-stone towards 12, (Scheme 16). The X-ray crystal structure (Fig. 1) of 64 has been determined, and in our estimate, it is still a promising candidate for cyclization to sumanene.$^{93}$

![Scheme 15](image)

An alternate approach$^{94}$ to sumanene 12 emanating from the terphenyl derivative 65 has also been devised and explored, (Scheme 17). Thus, 65 was subjected to FVP but, in this case too, only low yields of 64 and 66 (methyl group loss) was encountered. The terphenyl derivative 65 in turn was prepared through Suzuki cross-coupling between 2(2,5-dimethylphenyl) phenyl iodide and 2-methylphenylboronic acid.
Attempts were also directed towards a more embellished derivative of 12 e.g. the sumanene triketone 69, employing non-FVP conditions. For this purpose, the tris-bromomethyltriphenylene 63 was oxidized to 1,5,9-triformyltriphenylene 67 and further to the corresponding triacid 68, (Scheme 18). Efforts were now directed towards effecting triple cyclization in 68. However, when the triacid 68 was heated neat at 400°C, only mono-cyclized product 70 was produced, in which the remaining two carboxylic acid groups had decarboxylated. Attempted cyclization of triacid 68 with PPA or P2O5-methanesulfonic acid milieu gave the same product 70, (Scheme 19).

Disappointed by the observation that only monocyclization product 70 had been realized and that the decarboxylation had become a major impediment, we considered another approach to the functionalized sumanene system. We envisaged preparation of a functionalized coronene derivative e.g. 71, which through diazo transfer, could be transformed to the tris-aza-diazotriene 72. Photochemically or thermally induced three-fold Wolff rearrangement in 72 was expected to deliver the sumanene tricarboxylic acid 73, (Scheme 20). The tricarboxylic acid 73 could be either directly used for further evolution to higher 'bucky-bowls' or decarboxylated to the parent sumanene 12. Several exploratory studies were undertaken to give expression to the theme depicted in Scheme 20, however, preparation of the coronene derivative 71 has eluded us so far. These results have been detailed elsewhere.100,101

Scheme 16

Scheme 17

Scheme 18

Scheme 19

Scheme 20
Concurrently, several functionalization reactions on the mono- and di-bridged compounds 62 & 64 were investigated. It was possible to transform them to the corresponding mono-ketones, albeit in poor yield. These ketones were further subjected to pinacolic coupling reactions employing Ti(0) reagents to access higher order fragments of C₆₀. However, characterization of these compounds presented considerable difficulties and further efforts along these lines were abandoned.¹⁰⁰,¹⁰¹

Hemibuckminsterfullerenes 7 and 11

While several 'bowl-shaped' C₃₀H₈ hydrocarbons of different symmetry, representing half the carbon content of C₆₀ and embodying a significant motif on its surface are conceivable (7, 11 & 15 Schemes 1 and 74-76 in Scheme 21)¹⁰²-¹²² the C₃-hemibuckminsterfullerene 11 and C₂ᵥ-semi-fullerene 7, derivable from C₆₀ as shown in the retrosynthetic theme in Scheme 1 hold special appeal. Hemifullerene 11 of C₃-symmetry is unique in the sense that it alone can in principle dimerize to furnish C₆₀. (Schemes 2&3) Indeed, playing around with the metal complexes of 11 at high pressures to coax them into dehydrogenative dimerization to C₆₀ with metal encapsulation could be an exciting prospect! The C₂ᵥ-semi-fullerene 7 is a sort of corannuleno-corannulene and its boat-like shape is quite enchanting. Not surprisingly, 7 and 11 have received attention as synthetic targets and till date, these are the only two hemifullerenes that have succumbed to synthetic efforts.

\[ \text{Scheme 21} \]

C₂ᵥ-semi-fullerene 7

Rabideau et al.¹⁰² were the first to report the synthesis of 7 in 1995 following a variant of the Scott's seminal corannulene strategy. The 1,2,5,6-tetraoxopyracyene 77 (prepared via the benzylic oxidation of 1,2-dioxopyracyene 46) was elaborated through Knoevenagel condensation, bis-benzoannulation and chlorovinylation to 78. When 78 was subjected to FVP, four-fold cyclization occurred to furnish C₂ᵥ-semi-fullerene 7 in ~5% yield, (Scheme 22). Quantum mechanical calculations revealed a bowl-depth of 2.7Å for 7.

\[ \text{Scheme 22} \]

In 1996, the groups of Scott and Zimmernann,¹¹⁷ in a collaborative effort, accomplished a serendipitous looking synthesis of 7 via FVP of, bifluorenylidene derivative 80. The precursor 80 itself was obtained quite unexpectedly from cyclopenta[def]phenanthrene 79. Under high temperature conditions, ejection of cyclopenta-[def]phenanthrene moiety from 80 produces biradicals which subsequently cyclizes to give C₂ᵥ-semi-fullerene-7, (Scheme 23). It is worth noting that in both the approaches described above, the required hexagonal rings are built on two central pentagonal peripheries already present in the precursor, during the pivotal FVP step.

\[ \text{Scheme 23} \]

Recently, we have outlined a simple and conceptually new synthesis¹⁰³ of C₂ᵥ -semi-fullerene 7, wherein two pentagonal and one hexagonal rings are constructed in FVP step. According to this strategy, readily available m-xylene 81 on benzylic bromination was converted into 1-(bromomethyl)-3-methylbenzene 82, which was transformed into the corresponding ylide precursor 83. Wittig reac-
tion between 83 and m-tolualdehyde and further oxidative photocyclization furnished 2,7-dimethylphenanthrene 85 through olefin 84. This was transformed to the bis-ylide precursor 87 via the 2,7-bis(bromomethyl)-phenanthrene 86. Two fold Wittig coupling between the ylide derived from 87 and p-bromobenzaldehyde 88 furnished 89 as a mixture of E- and Z-stereo isomers which on oxidative photocyclization, furnished dibromodibenzopinacene 90 in a regioselective manner. FVP of 90 at 1150°C resulted in tandem three fold cyclization leading to the desired buckybowl 7. Under high temperature conditions, ejection of bromine atoms produces aryl radicals or benzene like intermediates which cyclize to form 7. Thus, through a sequence involving NBS bromination - Wittig olefination-photocyclization and pyrolysis, a simple aromatic compound like m-xylene can be elaborated into a complex, decacyclic, C2v- C30H12-aromatic bowl 7, (Scheme 24). 

C60 itself. Rabideau et al. were the first to report a synthesis106 of C7-symmetry 11 from commercially available indan-1,3-dione 91. Efficient acid mediated trimerization of 91 to tribenzo[afk]trine-none 92 (truxenetrione) is well known and the C27-trione served as the key building-block in this synthesis. gem-Dichlorovinylation of 92 furnished the hexachloro compound 93 with the retention of its symmetry. Partial dechlorination in 93 through metal-halogen exchange resulted in a mixture of tri- and tetra-chloro derivatives, which on FVP furnished hemi fullerene 11 in 10-15% yield, (Scheme 25).

Scheme 24

C7-Hemi fullerene 11 and Related Compounds
As mentioned above, C7-hemi fullerene 11, C30H12, is particularly an attractive target for synthesis as under appropriate conditions its cyclohydrogenative dimerization could lead to

Scheme 25

In 1997, Scott and Zimmermann disclosed a short synthesis117 of hemi fullerene 11 via FVP of a derivative of C7-tribenzo[cio]triphenylene 94. The precursor 94 was synthesized by a long but efficient route from α-tetralone. Regioselective bromination in 94 led to strategic placement of halogen substituents with the retention of the crucial C7-symmetry. Under FVP conditions, ejection of three bromine atoms from 95 through homolysis generated highly reactive aryl radical intermediates, which through 1,2-hydrogen shifts repositioned themselves for three-fold transannular bridging between peri-positions to furnish 11 (Scheme 26).
Preceeding the successful attainment of Scott and Zimmermann, several research groups had explored dehydrogenative cyclatization of C₃-tribenzotriphenylene 94 as a possible route to 11 but with only limited success. For example, Faust and Vollhardt¹¹⁴,¹¹⁵ made several attempts using both FVP and metal catalysis to promote transannular Ar-Ar coupling in 94 but 11 proved elusive and only mono- and di-bridged compounds, 96 and 97 could be characterized, (Scheme 27).

![Scheme 27](image)

Quite early in the race for 'bucky bowls', our research group also identified C₃-tribenzotriphenylene or its derivative as the ultimate precursor for C₃₀-hemifullerene 11. Our strategy in this context was two fold. We planned to develop a short and general synthesis of C₃-tribenzotriphenylene system so that a range of precursors could be readily assembled. Simultaneously, we also wanted appropriate substituents in position on the tribenzotriphenylene framework, which could serve as convenient handle for further elaboration, annulation etc. The key element of our approach was the endeavour to maintain the C₃-symmetry all the way from starting material to the target.

In our scheme of things, we identified C₃-symmetric 1,3,5-triformylbenzene 98 as the main building-block for quickly assembling the C₃-tribenzotriphenylene system and aimed at the C₃-trimethyl-hemifullerene 103 in which the symmetrically positioned methyl groups can be further exploited for accessing higher order fullerene fragments.¹¹⁸ Three-fold Wittig reaction between 1,3,5-triformylbenzene and the ylide derived from 2-methylbenzyl(triphenyl) phosphonium bromide, 99 followed by three-fold oxidative photocyclization furnished the desired 100. Although the yields were not very encouraging, the fact that six C-C bonds were formed and a heptacyclic ring system was put in place in just two steps and it was considered a very satisfying outcome. On activation under FVP conditions, 100 furnished monobridged compounds 101 and 102, which could be isolated and characterized, (Scheme 28). There was some indication of the formation of the dibridged compound as well but it could not be purified for characterization purposes. Not unexpectedly, extensive loss of methyl groups was observed in the FVP step. However, the desired 103 was not there.

![Scheme 28](image)

At this stage, we opted to play the halogen trick to promote transannular bridging in C₃-tribenzotriphenylene.¹¹³ This required incorporation of bromine substituents in the fjord region. Towards this end, three-fold Wittig reaction between 1,3,5-triformylbenzene 98 and the ylide derived from 4-bromophenyl-methyl (triphenyl) phosphonium bromide 104 was effected to furnish 105 as a mixture of E,Z isomers. Oxidative photocyclization in 105 was non-regioselective and led to the formation of the unsymmetrical 106 and the desired C₃-symmetric 107, (Scheme 29). When the C₃-symmetric tribromo tribenzotriphenylene, 107 was subjected to FVP, we were delighted to observe three-fold transannular cyclizations to deliver the coveted C₃-hemifullerene 11. The yield of 11 was abysmal by normal synthetic consideration but not too unusual for the three-fold pyrolytic ring closures in the fullerene series.¹⁷ A similar C₃-symmetry based approach towards hemifullerene 11 has been explored by Plater et al. They sought to employ hexafluorotribenzotriphenylene as the FVP precursor but difficulties in the purification of this compound proved a serious impediment. However, gas phase Argon ion mass spectrometric fragmentation of the impure sample containing hexafluorotribenzotriphenylene showed a mass peak at m/z 425(35%) attributable to symmetrically substituted trifluoro hemi-fullerene 11.
Acenaphthoindacenopicine ($C_{12}H_{12}$)

Rabideau and Clayton, closely following Scott's strategy towards the synthesis of corannulene, have disclosed the synthesis of acenaphtho [3,2,1,8-fghij] as indaceno [3,2,1,8,7,6-pqrstuv]picene indacenopicine 111, a $C_{32}H_{12}$ hydrocarbon, forming a sizable structural motif on the surface of both $C_{60}$ and $C_{70}$ (Scheme 30). In this approach, commercially available acenaphthenequinone 31 was condensed with the dibromo-ketone 108 to furnish 109. The resulting cyclopentadienone 109 on 4+2-cycloaddition with benzeyne and subsequent decarbonylation led to the benzo-annulated precursor 110. FVP of 110 furnished acenaphthoindacenopicine 111 in about 2.5% yield, (Scheme 30).

C$_7$-Triacenaphthotriphenylene ($C_{36}H_{12}$)

Progressive dismantling of $C_{60}$ along the $C_7$-symmetric route can also lead to $C_{36}H_{12}$-triacenaphthotriphenylene 113 which constitutes 60% of the carbon framework of $C_{60}$ surface. Scott et al. have observed that when commercially available decacyclene 112 is subjected to FVP at higher temperature regimes (1200-1300°C), three fold cyclized product 113 is obtained in about 0.2% yield along with singly closed $C_{36}H_{16}$ 115 and doubly closed $C_{36}H_{14}$ 114, (Scheme 31). A nice example of rich dividend accruing from persistence and experimental skills, as earlier efforts in this direction did not bear fruits. Apparently, at such high temperature conditions the molecule can circumvent the enormous amount of strain built up due to transannular bridging in FVP step. A crystal structure determination of 113 by Balch and co-workers has demonstrated a highly ordered columnar stacking of the bowls with the insertion of the convex face of one over the concave face of the other.

Synthetic Efforts Towards Higher Order [60]-Fullerene Fragments

There have been a few efforts directed towards higher order, deeper 'bowls', as well as at $C_{60}$ itself. We too have ventured into the arena. These efforts are summarized in this section.

Our successful acquisition of hemifullerene via an exceptionally short route spurred us to amplify the scope of our general strategy to higher order bowls. We chose $C_7$-tribenzohemifullerene 121, a $C_{42}H_{18}$ fragment of $C_{60}$ as our next target, as we felt that Scheme 32 could be readily adapted towards its synthesis. Likewise, $C_7$-symmetric triphenanthrotriphenylene 117 was identified as the precursor wherein key connectivities could be established through three-fold transannular cyclodehydrogenation under FVP conditions. A three-fold Wittig reaction between 1,3,5-triformylbenzene 98 and the ylide derived from 1-naphthylmethyl-(triphenyl)-phosphonium bromide 116 followed by oxidative photocyclization regime, furnished PAHs 117, 118 and 119 after extensive column chromatography. The structural identity of these products was gleaned through incisive NMR studies and the de-
sired C₃-symmetric isomer 117 turned out to be relatively minor photoproduct, (Scheme 32). It seems that while photoproduct 117 originates from the Z,Z,Z-form of Wittig product, compounds 118 and 119 are derived from the E,Z,Z-isomer. When the decacyclic C₃-symmetric 117 was subjected to FVP at 1150°C, only a monobridged product 120 could be realized from the pyrolysate which again demonstrates the limitations of unsubstituted planar PAHs towards transannular bridging under FVP conditions. Perhaps time again to deploy the halogen trick!

Scheme 32

Simultaneously, we also sought to adopt the salient features of Scheme 6 towards the C₃₀H₁₈ fragment 122 of C₆₀, for which the generalized retrosynthetic theme shown in Scheme 33 was considered quite promising.¹⁰⁰ Once again, the pivotal step was the three-fold Ar-Ar transannular connectivity in 123 under FVP conditions to furnish 122. The precursor 123 in turn, was sought to be accessed from 124 via oxidative photocyclization. (Scheme 33).

Towards the preparation of 124, a three-fold stereoselective Wittig reaction between 1,3,5-triformylbenzene 98 and 1-indanylttriphenylphosphonium bromide 125 was executed to furnish the tri-Wittig product 1,3,5-tris(1-indanyl)benzene 124 as a mixture of E,Z-isomers. (Scheme 34). Several attempts were made to induce cyclization in 124 to 123 employing photochemical and thermal regimes. However, all these efforts proved unsuccessful.

Considering that the configurational rigidity in 124 imposed by olefinic bonds could be a negative factor in promoting cyclization, it was saturated through catalytic hydrogenation. The hexahydrogenated product of 124 was also found to be unresponsive to thermal and photochemical activation, (Scheme 34).¹⁰⁰

The C₄₈H₁₂ fragment 126 of C₆₀, which is a tribenzo-fenced 'deep-bowl' of C₃-symmetry was chosen as our most formidable objective thus far. Retrosynthetic analysis on 126 along C₃-symmetry route, keeping in view our earlier tactics, led to the precursors 127 and 128. (Scheme 35). As a result of this, an exceptionally short route (3-steps) to the fragment 126 was envisioned, in which its 48-carbons were sought to be assembled in one step from commercially available starting materials like fluorene and mesitylene, through pre-installed complimentary functionalities, (Scheme 36).¹³⁴,¹³⁵

While several options were considered, Wittig reaction between 1,3,5-triformylbenzene 98 and ylide 129 was considered the most convenient way for directly delivering 128. Indeed, the three-fold Wittig reaction between 98 and 129 could be carried out through simple heating in chloroform to furnish the crystalline hydrocarbon 1,3,5-
tris(fluorenyldimethyl)benzene 128 in one step, (Scheme 36).

Elated by the ready access to the C_{48} compound 128 in one step, attention was immediately focused on its photocyclization to 127. However, despite many trials and variations in reaction conditions (temperature, solvent, filters), it was not possible to effect the 128 to 127 transformation. Disappointed by this outcome, we took recourse to thermal Ar-Ar coupling under FVP conditions as well as under Pd/C catalysis. However, no success was forthcoming. At this stage, X-ray crystal structure determination of 128 was undertaken, which indicated that the molecule was completely nonplanar and this precluded the possibility of cyclization under thermal or photochemical activation. The crystal structure (Fig.2) of 128 showed that the three fluorenyl units in it remain out of plane with respect to the central benzene ring and the molecule had a propeller-like structure with the dihedral angle between the central benzene ring and the three fluorenylidene moieties being 40°, 72° and 106°. There was no evidence of any twisting, folding or pyramidalization at the fluorenylidene double bond. Despite having several aromatic rings, the molecule possesses hardly any face-to-face π-π interactions but the crystal structure appears to be stabilized through CH...π interactions between the fluorenylidene moieties in a T-shaped geometry.\(^{134}\)

Recognizing that the failure of photocyclization in 128 was due to a sterically unfavourable situation, we sought to employ a more flexible framework which, in principle, could be an equivalent of a fluorene unit. This approach is indicated in the retrosynthetic theme shown in (Scheme 37).\(^{135}\)

Barbier-type reaction between 59 and a three-fold access of benzophenone in the presence of lithium was attempted and led smoothly to the assembly of 1,3,5-tris(2,2'-diphenyl-2'-hydroxyethyl)benzene, a C_{48} triol. The dehydration of the triol readily furnished 1,3,5-tris(2,2'-diphenyl-ethenyl)benzene 131 in good yield. The key step i.e., the three-fold Stilbene-type of photocyclization was now attempted to obtain the condensed aromatic product 134. However, the photocyclization chartered an unexpected but eventful course and the photo-product turned out to be 132 instead of 134. Although 132 was clearly an undesired product, it was felt that it could be serviceable for the limited purpose of Ar-Ar connectivity under thermal activation. Thermolysis of 132 under static conditions resulted in a rearrangement and aromatization through 1,2-phenyl migration to furnish 133 in good yield, (Scheme 38). These complicating, though interesting reactions, scuttled further efforts, towards 126 from 131 via 134 as contemplated in (Scheme 38).

Since the unexpected mode of photocyclization encountered above (131→132) was leading to an unwanted skeleton and consequent loss of symmetry, it was decided to circumvent this cyclization by blocking the unwanted photocyclization site. For this purpose, 1,3-bis(bromomethyl)-5-methyl-benzene 135 was reacted with benzophenone in the presence of lithium to effect a Barbier-type reaction. The resulting dial 136 could be readily dehydrated to 137. Gratifyingly, the key photocyclization step in 137 proceeded smoothly to deliver 138. Cyclodehydrogenation in 138 in Pd/C furnished the methano bridged compound 139, which could be further activated to a functionalized derivative 140, (Scheme 39). Although further cyclodehydrogenation on 139 were not successful under FVP conditions, yet the C_{35} motif of 139 and 140 represent a significant segment of C_{60}.\(^{135}\)

In one of the early efforts towards the synthesis of C_{60}-fullerene, Rassat et al. pursued the [C_{45}+C_{15}] approach and prepared fragment 142. The acid catalyzed trimerization of trindanone 141 resulted in the formation of trimeric compound 142, the C_{45}H_{48} product having 9 of the 12 pentagonal rings of C_{60} was obtained in 5% yield along with a dimer C_{30}H_{30} 143 (Scheme 40). However, further transformations on either 142 or 143 aimed at effecting appropriate cyclizations enroute to C_{60} were not very encouraging.\(^{124}\)

Chapman and Loguercio\(^{125}\) considered the triketone 144 as a possible fullerene precursor, which has 6 of the required 12 five-membered rings of C_{60}. The triketone 144 was synthesized from truxene lone 92, (Scheme 41). The X-ray crystal structure determination revealed that the triketone 144 is a severely distorted non-planar molecule and therefore not amenable to further cyclizations to furnish fullerene fragments.

Plater\(^{126}\) reported the assembly of an array of aromatic rings 146 via a simple acid catalyzed trimerization of methyl ketone 145 in 32% yield, (Scheme 42). In 145, one can readily visualize the right kind of connectivities to generate C_{60} (see arrows, shown on only one side). Under appropriate gas phase dehydrogenative conditions, 146
Scheme 41

1. 3-cyclopentenyl magnesium bromide
2. H₂SO₄, 95%
3. Thexyl borane, H₂O₂

Scheme 42

SiCl₄, 32% (or) Si(OEt)₄, 20%

Scheme 42a

147 (C₆₀H₆₀)

148 R₁ = H
      R₂ = H

Scheme 43

Scheme 44

syn - 152a
anti - 152b

syn - 152a Phenyl boronate ester
      + anti - 152b
      Pd(OAc)₂

153

155

FVP

154
could close like the petals of a flower to furnish C60. Despite the conceptual simplicity of this approach, success along this route has not been forthcoming.

It has been the expectation of some chemists that certain sixty carbon precursors, having a cage-like structure would have a propensity to collapse into C60 on appropriate activation. In this vein, interesting molecular entities like C60H60, 147 and C60H18, 148 have been synthesized by Vogtle130 and Rubin131,132 respectively. While their conversion to C60 is still awaited, acquisition of 147 and 148 is interesting in its own right.130-132 (Scheme 42a)

[70]-Fullerene Fragments

While noteworthy progress towards the synthesis of several C60 fragments has been achieved in the past few years,143,48 synthetic efforts towards the fragments of C70 4 have yet to make much headway.136 We recognized 'pinakene' 149, a C28H14 bowl-shaped hydrocarbon as a dominant sub-unit in C70 and have delineated its molecular structure, based on MNDO and MM2 calculations.40 In this context a possible synthetic approach to 149 was considered and 4,7,11,14-tetramethylidibenzof[g,h]napthacene 150 was identified as a key precursor. In a tacit reminiscent of our samunane approach, thermally induced four-fold transannular bridging under FVP conditions was envisaged, (Scheme 43).

An approach to 149 was contemplated involving Hart reaction137 between 2,5-dimethylphenylmagnesium bromide and 2,6-dichloroiodobenzene 151. Quenching the reaction with iodine furnished a mixture of configurationally stable iodoterphenyl derivatives, syn-152a and anti-152b from which the latter readily-crystallized and was identified through X-ray crystal structure determination (Fig. 3).

Palladium-catalyzed Suzuki cross-coupling reaction between 152 a,b and cyclic phenylboronate ester furnished a highly crowded m-terphenyl derivative 153 as a mixture of rotamers. Irradiation of 153 under conditions of oxidative photoelectrocyclization, to our surprise, furnished 4,7-dimethylidibenzof[g,h]napthacene 154, instead of the expected 150. Formation of 154 could involve an unprecedented photodearylation-rearylation process in which the p-xylene moiety in 153 is exchanged with a phenyl moiety from the solvent benzene prior to photocyclization. The driving force for the photodearylation 153 is the mitigation of steric strain and is probably manifested through the cleavage of one of the ArC—Car (CH3)2 bonds and rearylation through solvent capture. Alternatively, it is possible that 150 is indeed formed during the photo-irradiation, but suffers unprecedented loss of methyl groups to furnish 154. However, we have been unable to detect 150 in photolytate from 153.

The feasibility of the proposed transannular bridging was explored by subjecting the 4,7-dimethylidibenzonaphthacene 154 to flash vacuum pyrolysis. The only product isolated in this reaction was the mono-bridged compound 155 (~15% conversion), whose structure was revealed through the spectral data, (Scheme 44).138

Conclusion

Our project, directed towards a classical synthesis of C60-fullerene (bucky-ball) and its fragments (bucky-bowls) was one of the first major attempt of this kind anywhere. During the course of these endeavours considerable progress towards our stated objectives has been made. Corannulene 16 has been synthesized by a new and simple route. A novel synthetic approach to samunane 12, the heptacyclic C21H12 hydrocarbon, has been conceptualized and synthesis of seco-samunane, 64 has been accomplished. A new, general and exceptionally short strategy for assembling of a range of 'bucky-bowls' of C3-symmetry, consisting of Wittig reaction, oxidative photocyclization and flash vacuum pyrolysis (FVP), has been conceived. Through this approach two C60-hemifullerenes, the C2-symmetry 11 and C2v-symmetry 7 have been successfully synthesized and firm ground work for the synthesis
of C$_{42}$H$_{18}$, 121 and C$_{48}$H$_{12}$, 126 mapping extensively into the fullerene surface, has been laid. The stage is now set for a higher order assault towards the synthesis of C$_{60}$ and its siblings.

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