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Chemistry on a Half-Shell: Synthesis and Derivatization of Buckybowls

Andrzej Sygula^[a]**Keywords:** ((Keyword 1 / Keyword 2 / Keyword 3 / Keyword 4 / Keyword 5))

Buckybowls, bowl-shaped Polycyclic Aromatic Hydrocarbons structurally related to fullerenes, represent a class of hydrocarbons with unique properties and a potential for application as novel materials. This review outlines the development of the practical preparations of buckybowls, starting with the original synthesis of corannulene achieved in 1966. A particular attention is paid to the last decade developments which include construction of large,

highly nonplanar molecular networks (molecular clips and tweezers) capable of binding guest molecules of various sizes and shapes. In particular, such molecular clips were proven to form stable supramolecular complexes with fullerenes C₆₀ and C₇₀, both in solution and in the solid state.

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1. Introduction

In 1966 Barth and Lawton communicated a synthesis of a novel C₂₀H₁₀ [5]-circulene they named corannulene (**1**).^[1] Despite the unquestionable elegance of **1** to the time of Barth and Lawton report “this structure had neither adorned the jacket or end cover of any book nor served as a symbol of an international symposium”.^[2] More than that, the structure of corannulene had not appeared in the chemical literature prior to 1966 despite its relative simplicity and an obvious significance for the theory of aromaticity.



The arrangement of the benzene rings around the central (hub) five-membered ring induces a significant nonplanarity of the conjugated carbon network of **1** caused by the incompatibility of abutting pentagons and hexagons in the construction of the planar surfaces. As demonstrated by X-ray crystal structure determination the molecule adopts a form of a bowl with the depth of 0.87 Å, as defined by the distance between the planes defined by the central ring and by the ten rim CH carbon atoms.^[3] Therefore, corannulene as well as its larger analogs (buckybowls or fullerene fragments)^[4] introduce a novel structural motif to the chemistry and physics of Polycyclic Aromatic Hydrocarbons (PAHs) with the existence of non-equivalent concave and convex surfaces.

The original report attracted considerable attention to these novel systems but the chemistry and properties of corannulene were not investigated fully, due to its very limited supply. It has to be noted though that some important results were obtained i.e. the ¹H NMR

spectrum was reported, indicating the magnetic equivalence of all ten rim hydrogen atoms;^[1,2] some electrochemical studies showed a reversible reduction of **1** to its radical anion and presumably a dianion;^[5] and, most importantly, the X-ray crystal structure determination proved that corannulene is indeed bowl-shaped.^[3a]

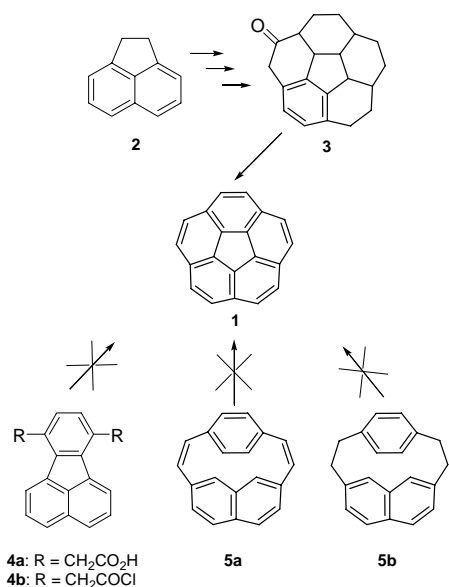
An interest in bowl-shaped conjugated carbon networks was dramatically renewed by the discovery of fullerenes due to the structural similarities of both families. Buckybowls are potential precursors for the rational synthesis of fullerenes and nanotubes. They can also be considered as model systems for studies of curvature vs. reactivity relationships. However, the scarcity of corannulene limited the studies of buckybowls since while quite impressive, the Barth and Lawton synthesis was too laborious to be repeated routinely in other laboratories. Clearly, more practical routes to buckybowls had to be found to allow their chemistry to flourish. This microreview summarizes the quest to improve synthetic methodologies for corannulene and the related species as well as the recent synthetic attempts to the construction of larger molecular architectures with corannulene subunits which can act as molecular clips and tweezers.

2. Synthesis of Corannulene

2.1. Original “Wet” Synthesis and Subsequent Failures

The curvature of corannulene is induced by the presence of a five-membered ring in its core. This feature introduces a significant strain caused by a distortion of the bond angles from the values usually found in planar benzenoid PAHs. It is therefore not surprising that the standard ring-closing synthetic procedures leading to the planar systems are less successful when applied to the synthesis of strained molecular bowls from the strainless precursors. Barth and Lawton original synthesis of corannulene started with acenaphthalene (**2**) and the remaining three six-membered rings were created one at a time by several synthetic steps to produce an intermediate **3**, which was subsequently reduced by sodium borohydride and aromatized over palladium on charcoal to give corannulene. This remarkable synthesis was achieved in 17 steps with the overall yield of 0.4%. (Scheme 1).^[1,2]

A search for alternative, more practical synthetic routes to **1** started immediately after the Barth and Lawton communication. Interestingly, some of the *failed* synthetic approaches were reported in the scientific literature probably reflecting a high interest in this novel system.^[6] Fluoranthene derivatives (**4**) were



Scheme 1. Top: Barth and Lawton synthesis of corannulene. Bottom: Some failed attempts to **1** reported in the literature.

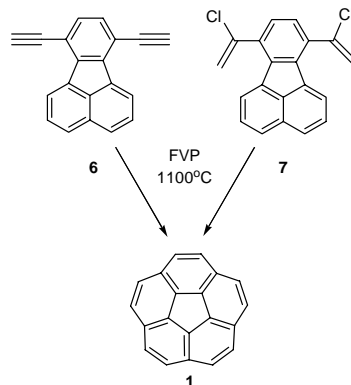
recognized as attractive precursors for **1**, since they possess four of the six rings of corannulene placed in the proper locations. However, despite numerous attempts, the Friedel-Crafts cyclization failed for both 7,10-fluoranthenediacetic acid (**4a**) and its corresponding acid chlorides (**4b**, Scheme 1).^[6a,b] These failures were attributed to the large distance between the carbon atoms expected to form the new bonds and to the rigid planar structure of the fluoranthene nucleus, which can be translated simply to the high activation barrier expected for the formation of the strained product from the strainless precursors. In a different approach, the corannulene core formation was attempted starting from cyclophanes **5a** and **5b**. Unfortunately, also in this case the formation of the central five-membered ring was not achieved under photochemical or thermal conditions.^[6c]

2.2. Flash Vacuum Pyrolysis: Gas Phase, High Temperature

A decisive break came in 1991 when Larry Scott and co-workers reported a successful formation of the corannulene core from 7,10-diethenylfluoranthene **6** under flash vacuum pyrolysis (FVP) conditions (Scheme 2).^[7] The synthesis represents a first practical route to corannulene. FVP is based on a brief exposure of the precursor evaporated or sublimed into a hot zone under vacuum (or a bleed of an inert gas) and the subsequent trapping of the products in a cold zone. The critical feature of Scott's approach appears to be high temperatures employed (ca. 1100°C), providing enough thermal energy to overcome high activation barriers for the intramolecular cyclizations. At the same time, the gas phase conditions minimize the undesired intermolecular side reactions.

Few years later the same research group reported an improved FVP-based synthesis of **1** with only three steps from commercially available precursors with an overall yield of 26%. The modified

version employed 7,10-bis-(1-chloroethenyl)fluoranthene (**7**) as the immediate FVP precursor for corannulene (Scheme 2).^[8] Presumably **7** is converted to **6** in the hot zone by elimination of two hydrogen chloride molecules.



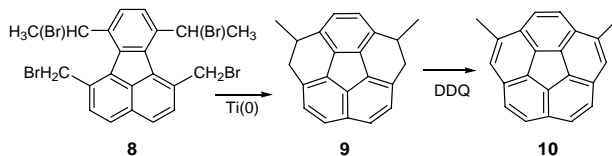
Scheme 2. Scott's FVP based syntheses of corannulene.

Several modifications of the FVP-based protocol have been proposed by various research groups but in most cases these routes do not offer any yield/efficiency improvement over the Scott's procedure.^[4]

2.3. Back to the Solution Phase Synthesis

FVP methodology has been indisputably successful in preparation of corannulene and other buckybowl. We will cover some of its applications in the synthesis of larger systems in Section 3. However, this high-temperature strategy suffers from several drawbacks. These include only modest yields for small buckybowl which drop dramatically for the larger systems, presumably due to the diminished volatility of the larger precursors. In addition, this technique has basically no functional group tolerance. Finally, FVP is difficult to be scaled up in a research laboratory. Therefore a need for more practical, large scale "wet" synthetic procedures became evident.

In 1996, 30 years after the Barth and Lawton synthesis, Jay Siegel reported the second successful solution-phase preparation of the corannulene core from tetrasubstituted fluoranthene precursor **8** (Scheme 3).^[9] The double ring closure leading to tetrahydroadimethylcorannulene **9** was achieved by low-valent titanium coupling. DDQ dehydrogenation of **9** produced 2,5-dimethylcorannulene in 18% combined yield of the two steps.

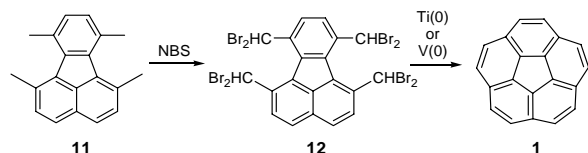


Scheme 3. Siegel's solution-phase synthesis of the corannulene core.

Notwithstanding the modest yield of the process this route to corannulene core represented an attractive alternative to the previous methods.

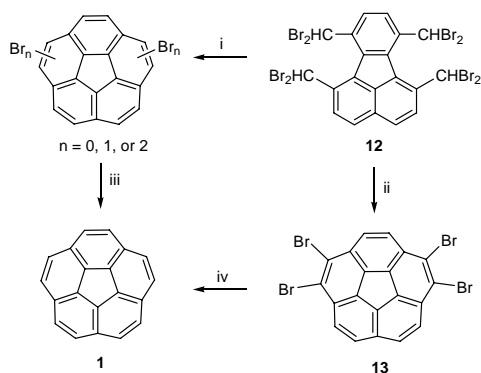
This synthetic route was subsequently improved independently by us and by Siegel's group.^[10,11] Radical bromination of 1,6,7,10-tetramethylfluoranthene **11** under forcing condition produced

octabromide **12**, which produces corannulene upon treatment with low-valent vanadium^[10] or titanium^[11] under high-dilution conditions (Scheme 4). In contrast to the previous method corannulene is formed from **12** without the intermediacy of tetrahydrocorannulene, so the extra dehydrogenation step is eliminated. The yields of the double ring closure step are quite impressive (70-80%).



Scheme 4. Corannulene synthesis by low-valent Titanium or Vanadium coupling of dibromomethyl groups.

In a continuing search for practical non-pyrolitic methods for buckybowl formation we attempted the hydrolysis of octabromide **12** so as to generate fluoranthene tetraaldehyde. However, reflux of **12** in acetone/water with sodium carbonate did not produce any aldehyde, but instead resulted in a formation of the corannulene core! Under these conditions a mixture of mono-, di- and tribromocorannulenes was produced (Scheme 5).^[12] The mixture can easily be debrominated to the parent **1** with 50-55% combined yield of the two steps. Replacing sodium carbonate with NaOH and changing the solvent to aq. dioxane resulted in a clean formation of a single product identified as 1,2,5,6-tetrabromocorannulene (**13**) in an impressive yield of 83% (Scheme 5).^[12]

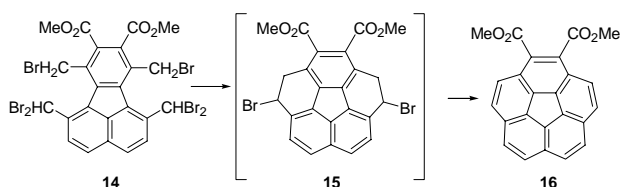


Scheme 5. Synthesis of corannulene by carbenoid coupling of dibromomethyl groups. (i) aq. acetone, Na₂CO₃, reflux, 3h. (ii) aq. dioxane, NaOH, reflux, 15 min. (iii) n-BuLi, THF, -78°C, 20 min, then dil. HCl. (iv) (a) Zn, KI, EtOH, 6 days or (b) Pd(OAc)₂, IMes.HCl, KOtBu, iPrOH, 30 min.

This serendipitously discovered procedure has several advantages in comparison with the previously described low-valent metal coupling methods which required strict oxygen- and moisture-free conditions, usage of expensive solvents and the application of lengthy high-dilution techniques. In contrast, the carbenoid coupling alternative not only dramatically reduces the cost but also simplifies the preparation which requires a brief reflux of the octabromide **12** in aqueous dioxane with some NaOH without need for inert gas atmosphere. In addition, the separation of the product is quite straightforward since tetrabromide **13** is rather insoluble in aqueous dioxane, so it is filtered, washed with water, and dried. The crude product is sufficiently pure to be

converted to parent corannulene or elaborated to rim-derivatized corannulenes without any further workup.^[12,13]

The formation of the corannulene core from polybrominated tetramethylfluoranthenes can also be achieved under milder conditions. Thus, 1,2-dicarbomethoxycorannulene **16** was synthesized in a respectable 60% yield from hexabromide **14** by the nickel powder double intramolecular coupling of the benzyl and benzyldene bromide groups.^[14] Nickel induced couplings of bromides have been widely used mostly for intermolecular couplings although some intramolecular couplings leading to the formation of ring systems have been reported as well.^[14] According to the postulated mechanism of such coupling the tetrahydrocorannulene dibromide **15** was the expected product of the intramolecular coupling of **14**. However, it is possible that a double HBr elimination occurs spontaneously under the reaction conditions leading to the rearomatized product **16**.



Scheme 6. Nickel powder induced formation of the corannulene core.

Considering the previous failed attempts to synthesize corannulene from 7-10-disubstituted fluoranthenes by solution Friedel-Crafts cyclizations it may seem surprising that the corannulene core can successfully be formed from 1,6,7,10-tetrasubstituted fluoranthene precursors under mild conditions. The success of the low-valent titanium coupling of the bromomethyl groups in **8** (Scheme 3) was originally attributed to the intermediacy of high energy organotitanium compounds since this methodology has been known to be effective for the formation of strained ring systems. However, no such argument could be used to explain the success of the carbenoid coupling route (Scheme 5). A closer look at the structural properties of 1,6,7,10-tetrasubstituted fluoranthenes reveals that they are severely strained in comparison to the 7,10-disubstituted analogs. X-ray crystal structure determinations exhibit a significant non-planarity of the fluoranthene core in both the parent tetramethylfluoranthene **11** and its tetrabromide **12** caused by the steric hindrance of the rim methyl or bromomethyl substituents.^[15] In contrast, the steric hindrance in 7,10-disubstituted fluoranthenes (**4b,b**) can be minimized by a rotation of the rim substituents away from the hydrogen atoms at C1 and C6 and/or out of the plane of the PAH's core. Simple MM2 modelling supports this explanation and suggests that while a significant strain is built during the cyclization of 7-10-disubstituted precursors to corannulene, the cyclization of 1,6,7,10-tetrasubstituted precursors releases some steric overcrowding and makes the final cyclization step feasible.^[16]

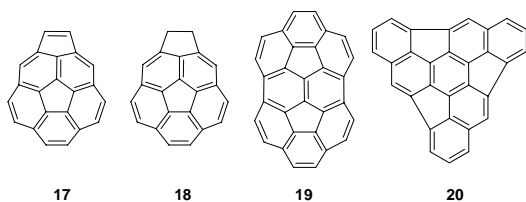
In summary, 30 years after the original corannulene report by Barth and Lawton, the practical synthetic procedures were developed which allow for preparation of **1** on a multigram scale and for employment of this exiting system as a starting material for the further elaboration.

3. Beyond Corannulene

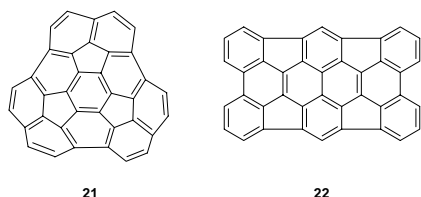
3.1. FVP Based Preparations of Larger Buckybowls

The successful Scott's synthesis of corannulene by FVP methodology resulted in a resurgence of interest in the synthesis of larger buckybowl. Using a modification of the Scott's procedure, our group prepared cyclopentacorannulene **17**, the first buckybowl besides corannulene to be synthesized.^[17] Introduction of the additional five-membered ring not only increased the curvature of the bowl but also dramatically increased its inversion barrier from the typical 11 kcal/mol for corannulene to 27.6 kcal/mol (measured for the acecorannulene **18**).^[18] In addition, **17** exhibits an interesting type of convex-concave π - π bowl stacking in the crystal, an arrangement which is not observed in corannulene.^[19]

We also succeeded in the synthesis of two isomeric "semibuckminsterfullerenes" ($C_{30}H_{12}$, **19**^[20] and **20**^[21]), i.e. buckybowl representing one half of the buckminsterfullerene carbon networks. These systems were latter prepared by others also employing FVP for the final step.^[22]



Even larger buckybowl like circumtriindene (**21**, $C_{30}H_{12}$)^[23] or **22**, ($C_{40}H_{14}$)^[24] have been prepared by the FVP methodology. Ultimately, formation of buckminsterfullerene C_{60} from a $C_{60}H_{27}Cl_3$ precursor was achieved by FVP.^[25] A recent review by Tsefrikas and Scott covers the FVP based preparations of buckybowl in a greater detail.^[4b]

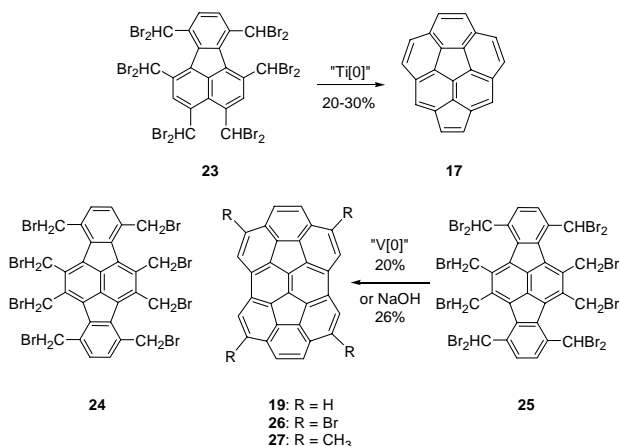


As we mentioned earlier, there are several drawbacks associated with the FVP approach. For example, while the yields for the pyrolytic formation of corannulene are satisfactory (30-40%), they drop dramatically for the larger buckybowl (usually less than 10%, sometimes even less than 1%). The following part of this microreview focuses on the more practical, non-pyrolytic methods of preparation of these large bowl-shaped molecular networks.

3.2. Non-Pyrolytic Preparations of Larger Buckybowls from Fluoranthenes and Related Precursors.

Cyclopentacorannulene **17** was originally prepared in our laboratory by FVP with a low 10-15% yield of the final step. Moreover, corannulene **1** was also formed as a byproduct of the pyrolysis and the separation of the two hydrocarbons proved to be difficult.^[17,19] The preparation of **17** was subsequently improved independently by us^[10] and Siegel^[11b] by employment of low-valent titanium coupling of hexakis(dibromomethyl)fluoranthene **23**. This solution phase synthesis produced **17** as the major product with a modest 20-30% yield (Scheme 7). We also succeeded to synthesize semibuckminsterfullerene **19** by a non-pyrolytic route.^[10] Thus, while low-valent titanium or vanadium coupling of octabromide **24** failed to produce any isolable amounts of **19** or its octahydro derivative, the same protocol applied to the

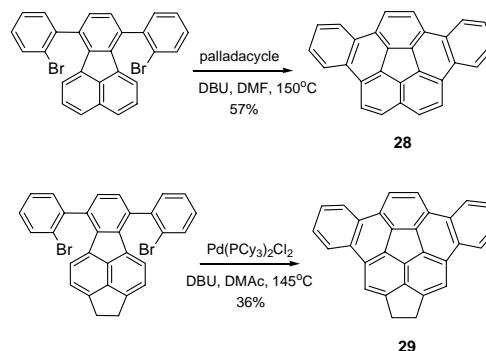
dodecabromide **25** produced **19** in a modest but respectable yield of 20% (Scheme 7).



Scheme 7. Non-pyrolytic preparations of cyclopentacorannulene **17** (top) and semibuckminsterfullerenes (bottom).

Latter we applied our base-induced carbenoid coupling to **25** to produce tetrabromo derivative **26** in a comparable 26% yield.^[26] Tetrabromide **26** was subsequently converted to tetramethylsemibuckminsterfullerene **27** which provided the first crystal structure of a semibuckminsterfullerene. In a full accord with our previous theoretical predictions, x-ray diffraction study of **27** showed that the pyramidalization of the two central carbon atoms of the C_{30} bowl is quite comparable to the pyramidalization of carbon atoms in buckminsterfullerene C_{60} .^[26]

Palladium-catalyzed intramolecular arylation reactions of 7,10-bis(2-bromophenyl)fluoranthenes offers another practical route to corannulene derivatives. The procedure, first reported by Scott for the synthesis of dibenzo[*a,g*]corannulene **28** in good 57% yield,^[27] was subsequently applied in our laboratory to produce more strained 1,2-dihydrocyclopenta[*b,c*]dibenzo[*g,m*]corannulene **29** in a modest 36% yield.^[28] Rim benzannulation of the cyclopentacorannulene core resulted in a slight flattening of its bowl, as evidenced by the X-ray crystal structure determination of **29**. As a result, the bowl-to-bowl inversion barrier of **29** was found by both dynamic NMR experiment (ca. 23.5 kcal/mol) and by theoretical calculations (19.3 kcal/mol, B3LYP/6-31G*) to be substantially lower than in the parent acecorannulene **18** (27.7 kcal/mol).^[28]



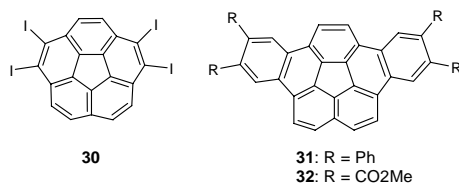
Scheme 8. Synthesis of dibenzocorannulenes **28** and **29** by intramolecular palladium-catalyzed arylation..

Similarly, rim benzannulation of the parent corannulene results in a lowering of the inversion barriers as observed by Scott and co-workers.^[29] Thus, dimethylcarbinol derivatives of benzocorannulene and dibenzo[*a,g*]corannulene have the inversion barriers of ca. 9.0 and <7.5 kcal/mol, respectively, slightly lower than the inversion barrier of 10.2 kcal/mol determined for the dimethylcarbinol derivative of corannulene.

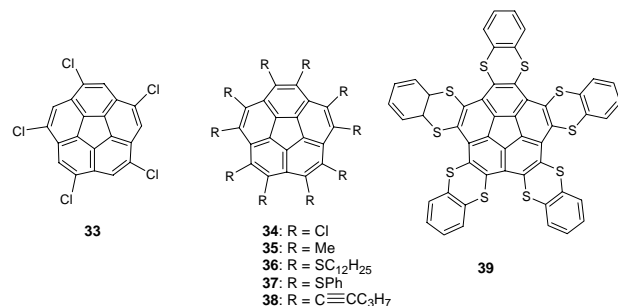
3.3. Corannulene as a Starting Material for Preparations of Larger Buckybowls

Availability of corannulene on a gram scale allowed for preparation of its several derivatives employing **1** as a starting material. The reader is referred to the recent review article by Wu and Siegel for the systematic coverage of the topic.^[4a] In the following paragraphs we will concentrate on the elaboration of the corannulenes leading to larger buckybowls or to the large molecular networks with corannulene subunits.

Rim halogenated corannulenes are attractive starting materials for further elaboration of the bowl. In this context tetrabromocorannulene **13**, the product of the base induced carbenoid intramolecular coupling of octabromide **12** (Scheme 5) is an easy to get precursor.^[12,16,30] Several rim substituted corannulenes have been prepared from **13** by various cross-coupling reactions. Tetraiodocorannulene **30** has also been prepared and used as a starting material for the synthesis of substituted dibenzocorannulenes **31** and **32**.^[16,30]



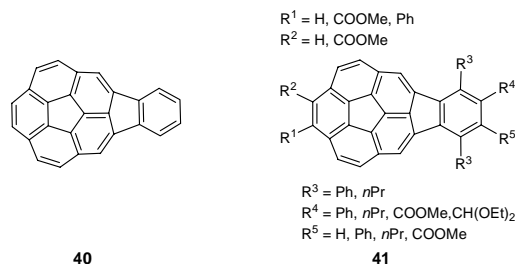
An interesting reaction between **1** and ICl discovered by Scott^[31] leads to *sym*-1,3,5,7,9-pentachlorocorannulene **33** in ca. 50% yield and opens a possibility for the construction of large molecular and supramolecular architectures of pentagonal symmetry. Numerous pentasubstituted corannulenes were prepared by cross-coupling reactions, mostly by Siegel and Scott research groups.^[4] More recently, Pappo and Keinan reported the synthesis of a number of *sym*-pentasubstituted corannulenes by employing **33** in high-yielding Suzuki coupling or Ullmann condensation reactions, including the formation of a third generation pentagonal dendrimer built on the corannulene core.^[32]



Perchlorination of corannulene under Balister conditions produced decachlorocorannulene **34**.^[33] This material, sparingly soluble in common organic solvents, is difficult to purify, but it has been used to prepare some highly-substituted corannulenes, e.g. decamethylcorannulene **35**,^[34] several decakis(alkylthio- or arylthio)corannulenes (e.g. **36** and **37**)^[35] and decapentynylcorannulene **38**.^[36] Decaalkynylcorannulenes like **38**

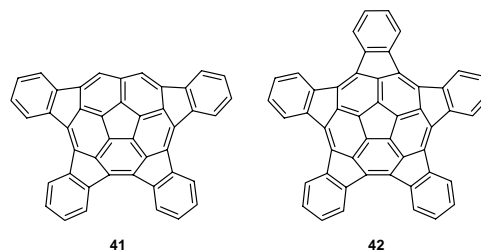
have a potential to form larger buckybowls via Bergman cyclization which could lead to a solution-phase synthesis of monodispersed single-walled carbon nanotubes. Unfortunately, no such cyclization was observed for **38** despite the favourable calculated energetics of the process.^[36]

Decachlorocorannulene was also employed as a starting material in the synthesis of the “fly trap” **39**. An X-ray crystal structure of **39** shows that two molecules of the “trap” capture a solvating molecule of benzene. In addition, **39** forms supramolecular complexes with fullerenes C₆₀ and C₇₀ in CS₂ with the NMR determined K_{assoc} of 1420 and 1080 M⁻¹, respectively.^[35]



Indenocorannulenes represent a natural expansion of the corannulene network toward the buckybowls representing larger parts of the fullerene surfaces. In addition to the enlargement of the bowl, introduction of the additional five-membered ring(s) increases the curvature of the molecular network. Indenocorannulene **40** was synthesized in 40% yield by a novel Suzuki-Heck coupling cascade reaction of pinacol corannuleneborate and *o*-dibromobenzene by Herrman, Scott and de Meijere.^[37] A series of highly substituted indenocorannulenes **41** was prepared by Siegel and co-workers utilizing a formal [(2 + 2) + 2] cycloaddition of 2,3-diakynylcorannulenes with acetylenes.^[38]

More recently Scott and Petrukhina research groups reported the solution phase synthesis and structural characterization of the whole family of indenocorannulenes, comprising monoidenocorannulene (C₂₆H₁₂) **40**, two isomeric diindenocorannulenes (C₃₂H₁₄), two isomers of triindenocorannulene (C₃₈H₁₆), tetraindenocorannulene **42** (C₄₄H₁₈) and pentaindenocorannulene **43** (C₅₀H₂₀).^[39] The synthesis started with Suzuki-Miyaura coupling of *o*-chlorophenylboronic acid with halogenated corannulenes and a subsequent ring closures by the microwave-assisted palladium-catalyzed intramolecular arylations.



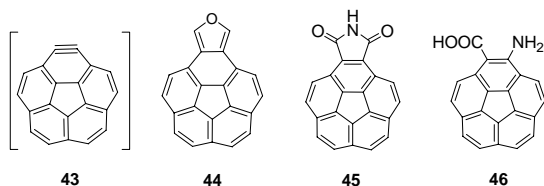
All these molecules map onto the geodesic network of C₆₀ and exhibit the increase in pyramidalization of the carbon atoms of the core with the increasing number five-membered rings. In fact, in five of the seven indenocorannulenes the maximum pyramidalization of the carbon atoms exceeds that of the carbon atoms in C₆₀.^[39]

In addition to their interesting structural properties indenocorannulenes like **42** may be considered as potential

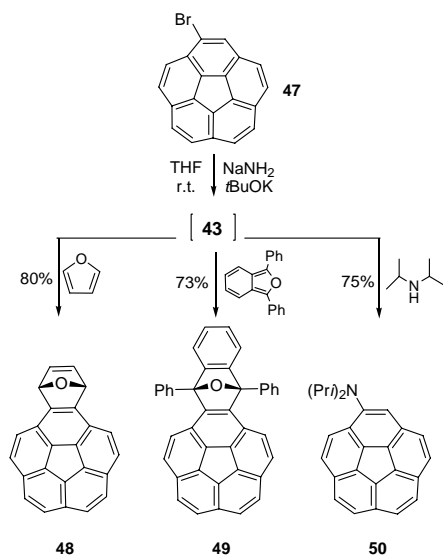
precursors for the synthesis of carbon nanotubes of uniform diameter.^[39]

3.4. Corannulene-based Synthons: Corannulyne and Isocorannulenofuran

Since the Diels-Alder cycloaddition reaction is often used to construct large conjugated systems we focused our attention on the previously unknown 1,2-didehydrocorannulene (corannulyne, **43**, a reactive dienophile), and the complementing diene, isocorannulenofuran (**44**). These building blocks promised an easy access to PAHs possessing corannulene subunits by the Diels-Alder methodology.



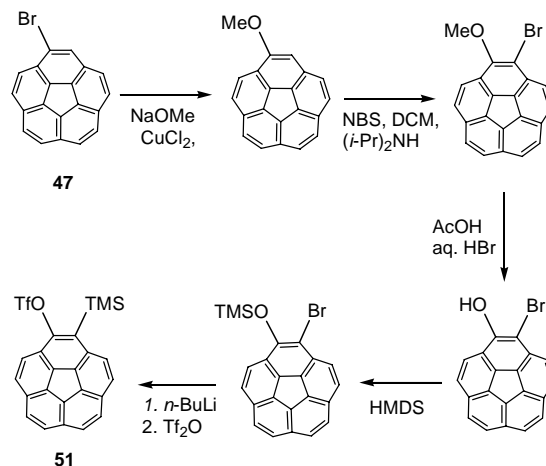
First, we attempted to generate **43** by the classic anthranilic acid route. Thus, imide **45** was synthesized from dimethyl 1,2-corannulene dicarboxylate (**16**) in a satisfactory yield but we failed to find a synthetically useful route to the desired amino acid **46**.^[40] We therefore looked for alternative methods of benzyne generation and tested the *ortho*-deprotonation of bromocorannulene **47** which is easily accessible through the bromination of corannulene. While our preliminary attempts employing alkyllithium bases failed, we discovered that **43** is indeed generated from **47** with sodium amide/potassium *t*-butoxide as a base. The generation of corannulyne was evidenced by the isolation of its adducts with furanes (**48**, **49**) and amines (e.g. **50**) with synthetically useful yields of 70 – 80% (Scheme 9).^[40]



Scheme 9. *ortho*-deprotonation induced generation of corannulyne **43** and its trapping by dienes and amines.

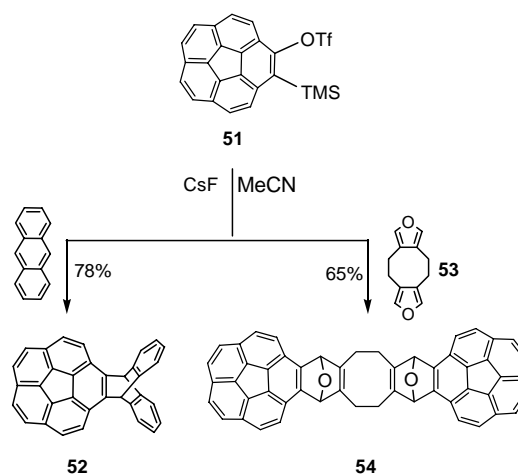
More recently we developed an alternative method for the generation of corannulyne under significantly milder conditions.^[41] The corannulyne precursor in this case is 2-TMS-corannulenyl triflate **51**. Recently developed procedures leading to *o*-TMS aryltriflates utilize appropriate phenols as the starting materials.^[42]

Unfortunately, hydroxycorannulene is not stable enough to serve as a starting material or an intermediate in the synthesis of **51**. After some experimentation we developed an alternative synthesis of 2-trimethylsilylcorannulene triflate (**47**) from bromocorannulene **47** in five steps (Scheme 10).^[41]



Scheme 10. Synthesis of *o*-trimethylsilylcorannulenyl trifluoromethanesulfonate (**51**).

The resulting *o*-TMS triflate **51** is stable enough to be stored for significant periods of time without any evidence of decomposition. On the other hand, **51** generates corannulyne under very mild conditions by simply stirring its solution in acetonitrile with CsF at room or slightly elevated temperatures as demonstrated by the formation of corannulyne adducts with furan (**48**, 85% yield) or anthracene (**52**, 78% yield).^[41] More recently we utilized **51** in a double Diels-Alder cycloaddition with difurane **53** to obtain a mixture of syn and anti isomeric products **54** with a combined 65% yield (Scheme 11).^[43]

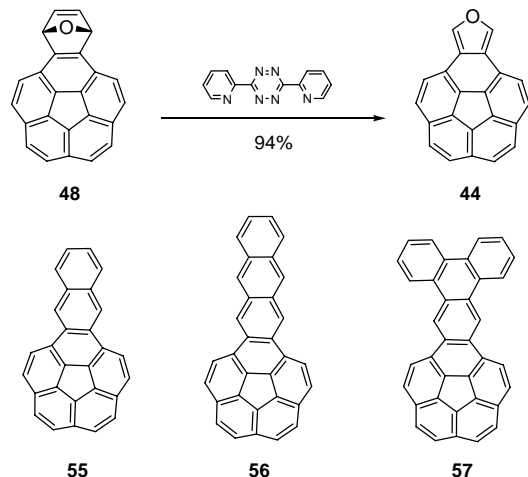


Scheme 11. Diels-Alder cycloaddition reactions of corannulyne generated from **51**.

While trapping corannulyne generated from **51** with furan produces adduct **48** in yields quite similar to that of our original base-induced *o*-deprotonation method (cf. Scheme 9), the two reactions shown in Scheme 11 represent the examples of processes we failed to complete with the base-promoted generation of corannulyne. These and other examples which we will discuss

later prove the versatility of *o*-TMS triflate **51** for the synthetically useful generation of 1,2-didehydrocorannulene. The extra labour required for the preparation of **51** pays off nicely in terms of a significant expansion of the scope of Diels-Alder cycloaddition and related reactions of corannulyne as compared to the original base-induced method.

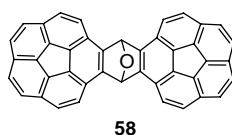
Availability of **48** opened the route to isocorannulenofuran **44** by the well-established “*s*-tetrazine approach”,^[44] which involved a brief heating of **48** with commercially available 2,6-bis-2-pyridyl-1,2,4,5-tetrazine in chloroform, followed by filtration of the purple reaction mixture through a plug of silica gel. This procedure provided isocorannulenofuran **44** in 94% yield (Scheme 12, top).^[45]



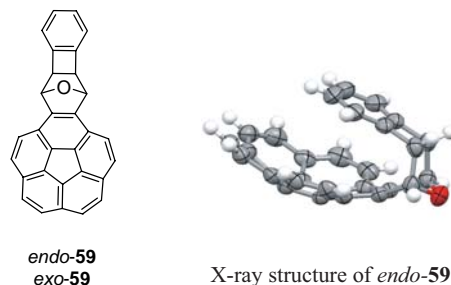
Scheme 12. (Top); Synthesis of isocorannulenofuran **44**. (Bottom): Some of the PAHs prepared by cycloaddition of benzynes to **44** followed by deoxygenation of the resulting endoxides.

While isobenzofurans are generally too unstable to be isolated, we were pleased to observe that **44** is one of the exceptions and can be isolated and fully characterized by NMR and MS and, more importantly, stored as a solid under inert atmosphere for prolonged periods of time without decomposition. On the other hand isofuran **44** is sufficiently reactive to give Diels-Alder cycloaddition products with dienophiles like benzynes. For example, **44** reacted with benzyne, 2,3-didehydronaphthalene and 9,10-didehydrophenanthrene to produce the respective 1,4-endoxides in 65 – 80% yields.^[45] Deoxygenation of the endoxides either with diiron nonacarbonyl or low-valent titanium (“Ti(0)”) provided hydrocarbons **55** – **57** in modest to good yields (Scheme 12, bottom). This methodology provides a synthetic route to extended PAHs which combine bowl-shaped corannulene subunits with planar fragments like naphthalene, anthracene and triphenylene.^[45]

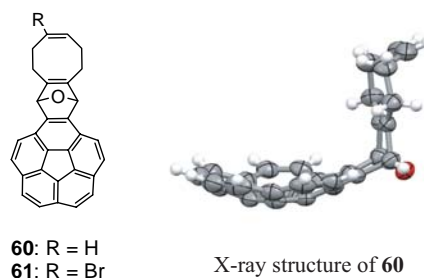
A successful Diels-Alder reaction between the corannulyne **43** and isocorannulenofuran **44** leading to the bis-corannulene adduct **58** represents a powerful example of the versatility of both *o*-TMS triflate as the aryne precursor and **44** as the diene. A mixture of **44** and **51** in MeCN/DCM was stirred at ca. 40 °C for 3 h with an excess of CsF resulting in a nearly quantitative formation of **58**.^[45]



We have also used isocorannulenofuran to generate highly nonplanar molecules with corannulene subunits. For example, **44** reacts with in situ generated bezocyclobutadiene to form a mixture of two isomeric adducts, *endo*- and *exo*-**59**. *Endo*-**59** exhibits an interesting highly nonplanar “closed-clam” structure, as determined by X-ray crystallography.^[43]



Similarly, isofuran **44** reacts with an excess of the reactive enynes generated by dehydrobromination of dibromo-1,5-cyclooctadienes producing a mixture of two adducts, **60** and **61**, with combined 78 % yield. Again, X-ray crystal structure determination of **60** shows an interesting “open-clam” arrangement with the six carbon atoms of the cyclooctadiene ring being almost coplanar and lying in a plane approximately perpendicular to the average plane of the corannulene subunit.^[43]



As can be seen from the previous paragraphs, the synthetic strategy for the preparation of larger molecular networks with embedded corannulene subunits developed and used in our laboratory is based on employment of the three methods outlined below:

Method 1, based on an introduction of highly sterically hindered 1,6,7,10-tetramethylfluoranthene subunit(s), followed by the radical bromination under forcing conditions which converts the dangling methyl groups to dibromo- or bromomethyl groups. Subsequent ring closures leading to the corannulene core formation is then achieved either by the base-induced carbenoid coupling or alternatively, by nickel powder induced intramolecular coupling.

Method 2, utilizes the Diels-Alder cycloaddition reactions of the appropriate dienes with corannulyne **43**, generated either from bromocorannulene **47** or from triflate **51**.

Method 3 also uses the Diels-Alder cycloaddition methodology but utilizes isocorannulenofuran **44**, a versatile, reactive diene in combination with the appropriate dienophiles.

4. Molecular Clips and Tweezers with Corannulene Pincers

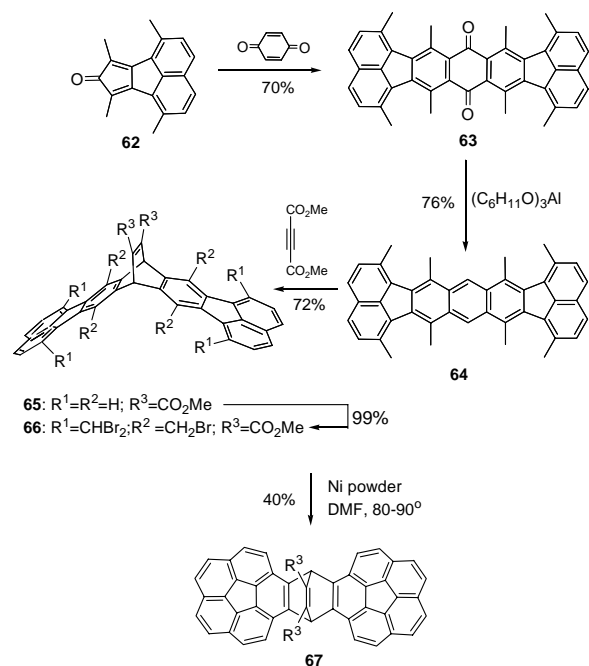
4.1. Buckybowls as Molecular Receptors for Fullerenes: A Potential

Buckybowls appear to be ideal candidates for molecular receptors for fullerenes with the potential ability to recognize curved-surfaces of the carbon cages through concave-convex “ball-and-socket” $\pi - \pi$ interactions. Such supramolecular motif was proposed some time ago to explain the formation of a radical cation of $[C_{60}@1]^+$ complex in the gas-phase, as detected by mass spectrometry.^[46] However, until 2007 no experimental evidence existed to unequivocally prove this supramolecular arrangement of buckybowls and fullerenes in condensed phases. Although the earlier NMR studies demonstrated the formation of supramolecular complexes of C_{60} with some pentakis- and decakis-substituted corannulenes, the reported association constants were relatively low and strongly substituent-dependent implicating that the majority of the binding could be attributed to the rim substituent-fullerene interactions in the complex.^[35,47] Thus, the early studies led to the conclusion that “the attractive force of the concave-convex interactions is not so significant, if at all” for these systems.^[48] Recent computational studies indicate that the binding energy of the supramolecular complex has to be quite significant to override significant entropy and solvation penalties associated with the formation of the complex. Apparently, dispersion-dominated attractive interaction of a single corannulene bowl with C_{60} is not strong enough for the dimer to be observed in solvents like toluene or CS_2 .^[49]

We therefore turned our attention to the design and synthesis of the larger systems with corannulene subunits prearranged in a proper way to overcome the aforementioned penalties. Obviously, the binding energy of a supramolecular assembly molecular receptor with the fullerene will be increased dramatically if more than one buckybowl “pincer” interacts with the guest. Also, the entropy penalties may be reduced if the pincers are pre-organized on the molecular scaffold (a tether) in an arrangement similar to their arrangement in the supramolecular assemblies.

4.2. Twin Corannulene: A Promise Unfulfilled

The first potential molecular clip with two corannulene pincers and the barrelene tether was synthesized some time ago in our laboratory employing *Method 1*.^[50] The synthesis shown in Scheme 13, started with a double Diels-Alder cycloaddition of cyclopentadienone **62** (an important intermediate in corannulene synthesis) to 1,4-benzoquinone to afford anthraquinone **63** in 70 %



Scheme 13. Synthesis of dicorannulenobarrelene dicarboxylate **67**.

yield. The anthraquinone was later reduced to anthracene **64** and subsequently converted to barrelene **65** by the cycloaddition with DMAD. Radical bromination of **65** under forcing conditions led to dodecabromide **66** which produced twin corannulene **67** with a respectable 40% yield by nickel-powder mediated intramolecular coupling of the bromomethyl and dibromomethyl groups.^[50]

Three distinct conformations of **67a-67c** are expected to exist and interconvert via the corannulene bowls inversions with relatively low energy barriers (Figure 1). Thus, at room temperature 1H NMR spectrum of **34** is quite simple due to the time-averaged C_{2v} symmetry of the molecule. In contrast, at low temperatures the presence of three different species with approximate populations of 82, 13 and 5% is revealed, in accord with the theoretical calculations predicting comparable energies of the three conformers. X-ray analysis reveals that **67** adopts the bis-exo conformation **67a** in the crystal, predicted by theory to represent the lowest energy conformation also in the gas-phase.^[50]

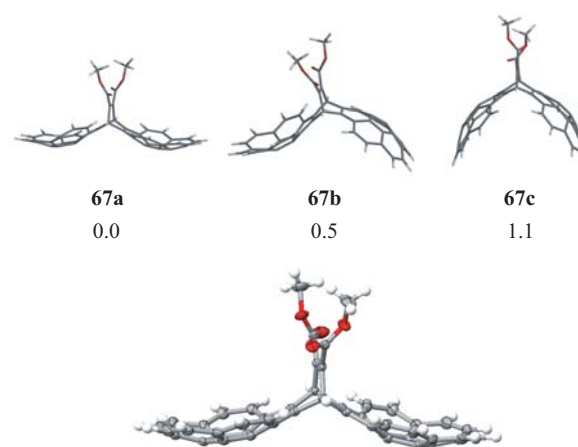
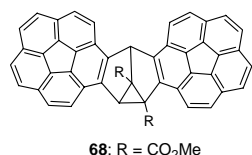


Figure 1. (Top) Relative energies [$kcal\ mol^{-1}$] calculated for the conformers of **67** at B3LYP/6-311G**//B3LYP/3-21G level. (Bottom) X-ray determined crystal structure of **67**. The solvating CCl_4 molecules are omitted for clarity.

Barrelene **67** looked like a legitimate candidate to act as a molecular receptor for fullerenes considering the presence of two corannulene pincers and a significant cavity formed between them. *Endo-endo* conformer **67c** appeared to be the best candidate to host C_{60} by a double concave dispersion interactions of the pincers with the convex surface of the carbon cage. Even though **67c** is slightly higher in energy than the remaining two conformers, its inclusion complex with C_{60} is calculated by MM2 to be significantly preferred over analogous complexes with either **67a** or **67b**. The same calculations predicted a significant binding energy for the $C_{60}@67c$ complex.^[50] Unfortunately, despite the computational predictions we were not able to detect any complexation of C_{60} with **67** experimentally. Attempts to co-crystallize of the two failed to produce any mixed crystals. Also, 1H NMR titration experiments did not show significant changes in the proton chemical shifts of **67** with increasing concentration of C_{60} , which indicates that K_{assoc} for the complex formation are small, at least in the tested solvents like toluene- d_8 , benzene- d_6 or CS_2 .^[50]

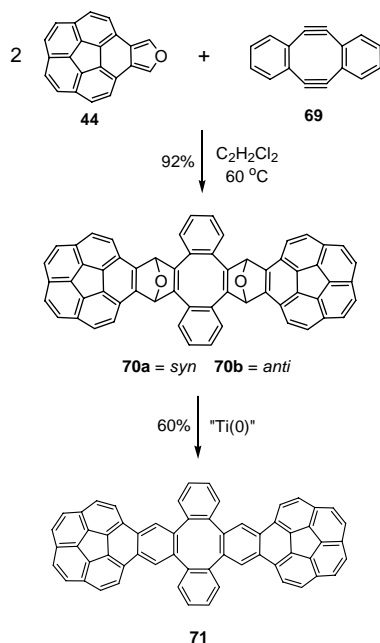
In contrast to most corannulene derivatives which are relatively stable and can be exposed to air and light without any noticeable degradation, barrelene **67** exhibited gradual changes of its NMR spectrum when exposed to light. In fact, a brief irradiation of its

solution with a sun lamp cleanly converted **67** to the isomeric dicorannulenobullvalene **68**.^[51] Although barrelene-semibullvalene rearrangements have been known since 1966, they are usually achieved under UV irradiation. We speculate that the unusual facility of **67** to photoisomerize under visible light irradiation may be due to better stabilization of the postulated biradical intermediates by the large corannulene subunits.



4.3. Buckycatcher: A Good Fit

More recently we prepared another molecular clip with two corannulene pincers with a tetrabenzocyclooctatetraene tether. The synthesis is outlined in Scheme 14.^[52] Isofuran **44** reacted with dibenzocyclooctadiene **69** producing a *ca.* 2:1 mixture of two isomeric adducts **70a** and **70b** with an excellent combined yield of 92% (*Method 3*). The adducts were separated and characterized for the identification purposes but upon deoxygenation by the low-valent titanium method they both were converted to the C₆₀H₂₈ hydrocarbon **71** ("buckycatcher") with good yields.



Scheme 14. Synthesis of buckycatcher **71**.

As in the case of **67**, **71** adopts a highly non-planar shape imposed by the tetrabenzocyclooctatetraene core. Bowl-to-bowl inversion of the corannulene pincers generates three conformers **71a-71c** which have very similar stabilities (Figure 2).^[52] Quite recently we realized that a fourth conformation **71d** is also possible due to some flexibility of the tether which allows for the intramolecular π - π concave-convex stacking of the corannulene pincers.^[53] At the highest level of theory applied (B97-D/cc-pVQZ) **71d** represents the global minimum conformation of **71**. Apparently the dispersion stabilization of the stacked pincers overcomes the energy penalty caused by a significant distortion of the tether from its lowest energy conformation.

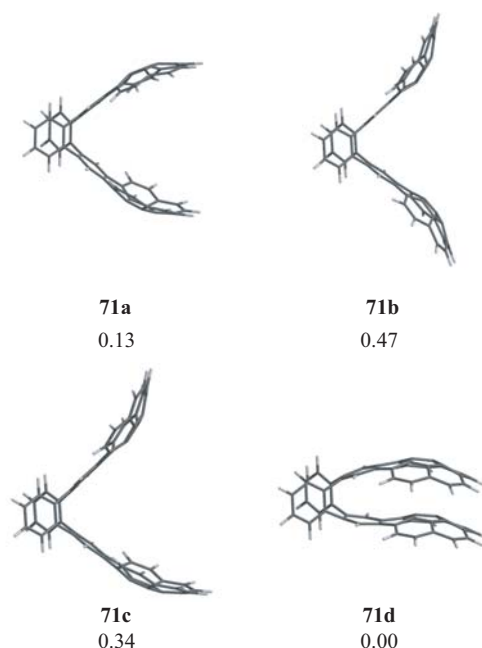


Figure 2. Relative energies [kcal mol⁻¹] calculated for the conformers of **71** at B97-D/cc-pVDZ level.

It has to be pointed out that the calculated relative stabilities of all four conformers lie in the range of 0.5 kcal mol⁻¹ only, so it is hard to declare with certainty which conformer is the most stable in the gas phase.^[53] Considering that the energy barriers for the interconversion are relatively low and thermally accessible at ambient temperatures, the conformational equilibria expected to be strongly influenced by solvation and/or complex formation with various guest molecules, will be established quickly.

Slow evaporation of an approximately equimolar solutions of **71** and C₆₀ in toluene produced dark red mixed crystals. To our delight X-ray crystal structure determination revealed that an inclusion complex C₆₀@**71** was formed (Figure 3).^[52]

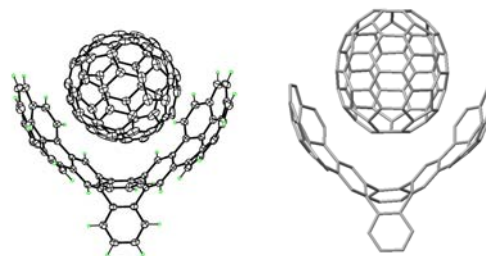


Figure 3. (Left):Ortep representation of the C₆₀@**71** inclusion complex. The solvating toluene molecules are omitted for clarity. (Right):The crystal arrangement of C₇₀ and **71**. Hydrogen atoms of **71** and two solvating PhCl molecules are not shown.

C₆₀@**71** exhibits all structural characteristic anticipated for **71** acting as a molecular clip for the guest C₆₀. The fullerene molecule is placed nicely in the center of a doubly-concave cleft formed by the corannulene pincers. All of the corannulene subunits carbon atoms are in van der Waals contact with the fullerene cage with the shortest distance of 3.128 Å. Both **71** and C₆₀ lie on a crystallographic mirror plane which relates the two corannulene subunits.

Complexation of C_{60} with buckycatcher **71** also takes place in solution. An NMR titration experiment in deuterated toluene exhibited systematic downfield shifts for the four symmetry independent protons of the corannulene subunits with increasing concentrations of C_{60} . A high binding constant $K_a = 8600 \pm 500 \text{ M}^{-1}$ was determined by non-linear curve fitting of the NMR data.^[52]

More recently we also determined the association constant for the formation of an inclusion complex of C_{70} with buckycatcher.^[53] In toluene- d_8 the association constant $K_a = 8600 \pm 500$ was determined by the NMR titration experiment. This number is lower than the analogous value found for C_{60} @**71**. However, both association constants provide very similar free enthalpies ($-5.1 \text{ kcal mol}^{-1}$ C_{70} @**71** and $-5.3 \text{ kcal mol}^{-1}$ for C_{60} @**71**) indicating the lack of significant specificity of buckycatcher in molecular recognition of the two carbon cages. Same conclusion was drawn from our computational study which found similar binding energies for both inclusion complexes.^[53]

Single crystals were grown from the mixed solutions of C_{70} with buckycatcher in various solvents. Despite several attempts, we failed to obtain acceptable results from X-ray crystal structure determinations due to crystal defects and/or multiple disorder problems. However, the crude results from these studies confirm the presence of 1:1 inclusion complexes of buckycatcher with C_{70} and the basic structure obtained for C_{70} @**71***2PhCl demonstrated that the oblong C_{70} cage interacts with the buckycatcher's corannulene pincers in a fashion closely resembling C_{60} @**71** complex (Figure 3).^[54]

In conclusion, buckycatcher **71** proved to be a very efficient molecular clip for both C_{60} and C_{70} . The formation of stable inclusion complexes in both solution and the solid state provided the first experimental evidence for the importance of concave-convex π - π stacking in the supramolecular chemistry of buckybowl and fullerenes.

A number of computational studies appeared in literature using C_{60} @**71** complex as a model system for the assessment of the effectiveness of the dispersion interactions of the large conjugated non-planar carbon networks as well as to assess the potential application of the supramolecular assembly as a novel class of electronic materials.^[49,53,55] Although the calculated binding energies of C_{60} with buckycatcher significantly depend on the computational model, all these studies describe C_{60} @**71** as a typical van der Waals complex bound primarily by London dispersion forces with no specific electrostatic, orbital or charge transfer interactions. The same conclusion was reached basing on an energy decomposition analysis of the bonding in C_{70} @**71** complex.^[53]

The „best theoretical estimate“ of the binding energy in C_{60} @**71** lies in the range of $36\text{--}40 \text{ kcal mol}^{-1}$.^[49,53,55] The experimental ΔG_{293} determined for the complex formation in toluene is $-5.3 \text{ kcal mol}^{-1}$ only.^[52] This dramatic difference illustrates the severe entropy and solvation penalties associated with the supramolecular formation. Since the binding energy of a simpler C_{60} @**1** assembly is more than two-times lower than in C_{60} @**71** it is not surprising that the formation of C_{60} @**1** has not been detected in solution since the aforementioned penalties will surely override the binding and make the complex formation strongly endergonic.^[49]

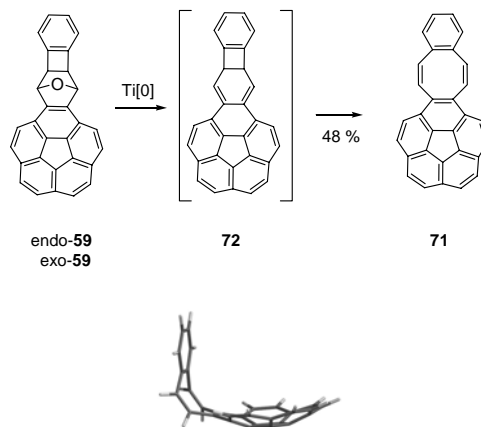


C_{60} @**1**

On the other hand the convex-concave π - π stacking arrangement was recently observed by Fasel, Siegel and co-workers in the surface-supported supramolecular architectures obtained by deposition of C_{60} onto a monolayer of corannulene adsorbed on the Cu(110) surface.^[56]

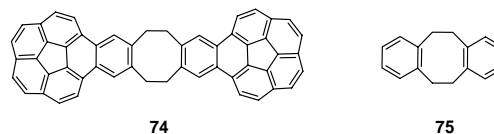
4.4. Potential Molecular Clips with Corannulene Pincer(s) and More Flexible Cyclooctatetraene or Cyclooctadiene Tethers

A series of highly nonplanar systems with clefts of various sizes and shapes constructed by combining corannulene and cyclooctadiene (COD) or cyclooctatetraene (COT) subunits was recently synthesized and characterized by X-ray crystal structure determination.^[43] Two of the systems (**59** and **60**) were mentioned previously in this micoreview. In addition, deoxygenation of the endoxides *exo*- and *endo*-**59** resulted in formation of $C_{30}H_{16}$ hydrocarbon **72** in a modest 48% yield, presumably through the dihydrobiphenylene intermediate **73** (Scheme 15). The target **72** has not been characterized by X-ray crystallography but it is expected to form an “open-clam” clip with corannulene and benzene pincers located on the tub-shaped COT tether.^[43]



Scheme 15. Synthesis of **72** and its B3LYP/6-31G* calculated structure.

We also prepared a more structurally flexible clip **74** with two benzocorannulene pincers and 1,5-cyclooctadiene tether with interesting conformational behavior. As we mentioned previously, **51** was employed as a corannulene precursor in a double Diels-Alder cycloaddition to difuran **53** to produce a mixture of two isomeric bis-endoxides **54** (see Scheme 11). Low-valent titanium deoxygenation of **54** provided the desired $C_{52}H_{28}$ hydrocarbon **74** in 60% yield.^[43]



Conformational flexibility of COD tether allows for an adoption of conformations unavailable for the more rigid tetrabenzoCOT core of buckycatcher **71**. We studied the conformational preferences of **74** by both Molecular Mechanics and DFT methods and compared the results with a simpler dibenzocyclooctadiene analog **75**, which has been previously studied by both theory and experiment. Basing on these studies we considered three conformations of the central COD ring in **74**, i.e. twist boat (TB), chair (C) and twist (T) (Figure 4).^[43]

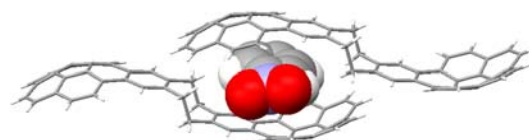
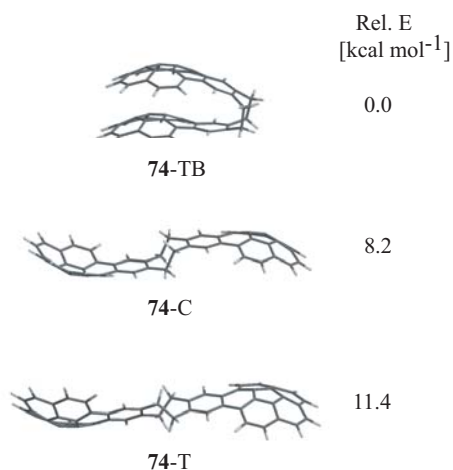


Figure 4. Crystal structure arrangement in **74***PhNO₂ solvate. The second molecule of **74** is added to show the encapsulation of the solvating nitrobenzene molecule.

Figure 4. B3LYP-D/TZVP calculated geometries and relative energies of the three conformations of COD core in **74**.

Conformational preferences in **74** are quite different from the dibenzo analog **75**. Previous low temperature NMR studies revealed the existence of two conformers of the latter, i.e. **75**-TB and **75**-C, in comparable amounts and, accordingly, theoretical studies predict the energies of the two conformers to be quite similar, with the twist **75**-T having significantly higher energy which precludes its detection by NMR experiment (0.0, 0.2 and 3.5 kcal mol⁻¹ at B3LYP-D/TZVP level). In contrast, twist-boat conformer **74**-TB is dramatically more stable than the two others (Figure 4), apparently due to its stabilization by intramolecular concave-convex π - π stacking of the corannulene pincers. The π - π stacked **74**-TB resembles buckycatcher conformer **71d** (Figure 2) but the higher flexibility of the tether in **73** allows for a more efficient overlap of the corannulene pincers and, as a result, a stronger preference for the TB conformation.^[43]

In contrast to other corannulene-based molecular clips synthesized in our laboratory, **74** has a very limited solubility in organic solvents, significantly lower than that of the larger and less flexible buckycatcher **71**. The strong preference for the internally π - π stacked **74**-TB conformation may explain its low solubility in common organic solvents since the solvent-accessible surface of this conformation is dramatically reduced in comparison to the “open” conformations of other buckybowls. On the other hand an interesting possibility arises that the “open” conformations like **74**-C could become preferred in condensed phases if the solvating power of a solvent can override the strong gas-phase preference for **74**-TB. We were not able to address this problem by low-temperature NMR studies due to the very limited solubility of **74**. Also, several attempts to grow X-ray quality crystals from weakly solvating solvents failed. On the other hand we obtained good quality crystals of a 1:1 solvate of **74** with nitrobenzene and the X-ray structure determination showed that the “open” chair conformation **74**-C prevails in the solid state of the solvate (Figure 5). Even in the “open” conformation **74** acts as a host since the solvating nitrobenzene molecule is encapsulated by two neighboring molecules of **74** and is in van der Waals contacts with the concave sides of the benzocorannulene pincers.^[43]

Despite the observation of the chair conformation of **74** in the solid state of its solvate we strongly believe that the isolated or weakly solvated molecule will prefer the TB conformation since it is calculated at the very reliable level of theory to be by far more stable than the “open” conformation. Clearly, the solvation effects constitute a decisive factor for the chair conformational preference in the nitrobenzene solvate. We are still pursuing experimental evidence for the existence of the “closed” conformation of **74**.

5. Conclusions

It took 25 years for the original laborious synthesis of corannulene to be substituted by an alternative, simpler FVP-based preparation. Another 10 years passed before practical solution-phase syntheses were discovered allowing corannulene to be produced on a multigram scale. Due to this progress corannulene can now be employed as a starting material for the construction of larger nonplanar carbon networks.

Several novel PAHs with corannulene subunits have been synthesized and characterized, extending our basic understanding of the nature of aromaticity “in three dimensions” as well as promising a development of a new class of materials with unique properties. For example, the extended corannulenes are potential starting materials for a solution-phase synthesis of monodispersed carbon nanotubes and/or fullerenes other than C₆₀ and C₇₀. Several polysubstituted corannulene derivatives exhibit unique fluorescent and electrochromic properties that can be applied in organic light emitting diode technology. Also, due to low-lying unoccupied molecular orbitals, buckybowls have a high capacity for alkali metal doping, with a potential for utilization as energy storage systems (batteries) if approaches can be developed to deal with the high reactivity of such systems. When properly tethered, the buckybowl pincers can effectively encapsulate host molecules of various shapes and sizes, including fullerenes. These molecular clips and tweezers can act as chemical sensors or can be applied in separation sciences. Also, recent theoretical studies predict host-guest fullerene@buckycatcher complexes to be both two-photon absorption active and charge-transfer mediating materials with intriguing applications in nanoelectronic devices.

With recently developed procedures (and new ones surely to be discovered) the synthesis of buckybowls is no longer the seriously limiting factor for research. We are sure that the novelty of buckybowls and their unique properties will continue to attract the attention of chemists and material scientists. We look forward to the exciting results of future research.

Acknowledgments

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collaboration with Professor Peter W. Rabideau in the area of novel PAHs requires my special appreciation.

((Author
Portrait))

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- [1] W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1966**, *88*, 380-381.
- [2] W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1971**, *93*, 1730-1745.
- [3] a) J. C. Hanson, C. E. Nordman, *Acta Cryst. B.* **1976**, *B32*, 1147-1153; b) M. A. Petrukhina, K. W. Andreini, J. Mack, L. T. Scott, *J. Org. Chem.* **2005**, *70*, 5713-5716.
- [4] For the recent reviews see: a) Y.-T. Wu, J. S. Siegel, *Chem. Rev.* **2006**, 4843-4867; b) V. M. Tsefrikas, L. T. Scott, *Chem. Rev.* **2006**, *106*, 4868-4884. (c) A. Sygula, P. W. Rabideau in *Carbon Rich Compounds*; (Eds.: M. M. Haley, R. R. Tykwinski), Wiley-VCH: Weinheim, **2006**, pp. 529-565.
- [5] J. Janata, J. Gendell, C.-H. Ling, W. E. Barth, L. Backes, H. B. Mark Jr., R. G. Lawton, *J. Am. Chem. Soc.* **1967**, *89*, 3056-3058.
- [6] a) J. T. Craig, M. D. Robins, *W. Aust. J. Chem.* **1968**, *21*, 2237-2245; b) R. H. Jacobson, PhD Dissertation, University of California, Los Angeles, 1986; c) J. R. Davy, M. N. Iskander, J. A. Reiss, *Tetrahedron Lett.* **1978**, 4085-4088.
- [7] L. T. Scott, M. M. Hashemi, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1991**, *113*, 7082-7084.
- [8] L. T. Scott, P.-C. Cheng, M. M. Hashemi, M. S. Bratcher, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1997**, *119*, 10963-10968.
- [9] T. J. Seiders, K. K. Baldrige, J. S. Siegel, *J. Am. Chem. Soc.* **1996**, *118*, 2754-2755.
- [10] A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1999**, *121*, 7800-7803.
- [11] a) T. J. Seiders, K. K. Baldrige, E. L. Elliott, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **1999**, *121*, 7439-7440; b) T. J. Seiders, E. L. Elliott, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **1999**, *121*, 7804-7813.
- [12] A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **2000**, *122*, 6323-6324.
- [13] P. Bachavala, M. S. Thesis, Mississippi State University, Mississippi State, 2006.
- [14] A. Sygula, S. D. Karlen, R. Sygula, P. W. Rabideau, *Org. Lett.* **2002**, *4*, 3135-3137.
- [15] a) A. Borchardt, K. Hardcastle, P. Gantzel, J. S. Siegel, *Tetrahedron Lett.* **1993**, *34*, 273-276; b) A. Sygula, F. R. Fronczek, P. W. Rabideau, *Tetrahedron Lett.* **1997**, *38*, 5095-5098.
- [16] A. Sygula, G. Xu, Z. Marcinow, P. W. Rabideau, *Tetrahedron* **2001**, *57*, 3637-3644.
- [17] A. H. Abdourazak, A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1993**, *115*, 3010-3011.
- [18] A. Sygula, A. H. Abdourazak, P. W. Rabideau, *J. Am. Chem. Soc.* **1996**, *118*, 339-343.
- [19] A. Sygula, H. E. Folsom, R. Sygula, A. H. Abdourazak, Z. Marcinow, F. R. Fronczek, P. W. Rabideau, *Chem. Commun.* **1994**, 2571-2572.
- [20] P. W. Rabideau, A. H. Abdourazak, H. E. Folsom, Z. Marcinow, A. Sygula, R. Sygula, *J. Am. Chem. Soc.* **1994**, *116*, 7891-7892.
- [21] A. H. Abdourazak, A. Z. Marcinow, A. Sygula, R. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1995**, *117*, 6410-6411.
- [22] a) S. Hagen, M. S. Bratcher, M. S. Erickson, G. Zimmermann, L. T. Scott, *Angew. Chem., Int. Ed.* **1997**, *36*, 406-408; b) G. Mehta, G. Panda, *Chem. Commun.* **1997**, 2081-2082; c) G. Mehta, G. Panda, P. V. V. S. Sarma, *Tetrahedron Lett.* **1998**, *39*, 5835-5836.
- [23] a) L. T. Scott, *Angew. Chem. Int. Ed.* **2004**, *43*, 4994-5007; b) L. T. Scott, M. S. Bratcher, S. Hagen, *J. Am. Chem. Soc.* **1996**, *118*, 8743-8744.
- [24] L. Peng, Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2006.
- [25] L. T. Scott, M. M. Boorum, B. J. McMahon, S. Hagen, J. Mack, J. Blank, H. Wegner, A. de Meijere, *Science* **2002**, *295*, 1500-1503.
- [26] A. Sygula, Z. Marcinow, F. R. Fronczek, I. Guzei, P. W. Rabideau, *Chem. Commun.* **2000**, 2439-2440.
- [27] H. A. Reisch, M. S. Bratcher, L. T. Scott, *Org. Lett.* **2000**, *2*, 1427-1430.
- [28] Z. Marcinow, A. Sygula, A. Ellern, P. W. Rabideau, *Org. Lett.* **2001**, *3*, 3527-3529.
- [29] a) C. C. McComas, B. S. Thesis, Boston College, Chestnut Hill, MA, 1996; b) M. S. Bratcher, M. S. Thesis, Boston College, Chestnut Hill, MA, 1996.
- [30] G. Xu, A. Sygula, Z. Marcinow, P. W. Rabideau, *Tetrahedron Lett.* **2000**, *41*, 9931-9934.
- [31] a) P. Cheng, Ph. D. Dissertation, Boston College, Chestnut Hill, MA, 1996; b) L. T. Scott, *Pure Appl. Chem.* **1996**, *68*, 291-300.
- [32] a) D. Pappo, T. Mejuch, O. Reany, E. Solel, M. Gurram, E. Keinan, *Org. Lett.* **2009**, *11*, 1063-1066; b) R. Gershoni-Poranne, D. Pappo, E. Solel, E. Keinan, *Org. Lett.* **2009**, *11*, 5146-5149.
- [33] S. Samdal, L. Hedberg, K. Hedberg, A. D. Richardson, M. Bancu, L. T. Scott, *J. Phys. Chem.* **2003**, *107*, 411-417.
- [34] T. J. Seiders, K. K. Baldrige, E. L. Elliott, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **1999**, *121*, 7439-7440.
- [35] a) M. Bancu, A. K. Rai, P.-C. Cheng, R. D. Gilardi, L. T. Scott, *Synlett* **2004**, 173-176; b) P. E. Georghiou, A. H. Tran, S. Mizyed, M. Bancu, L. T. Scott, *J. Org. Chem.* **2005**, *70*, 6158-6163.
- [36] T. Hayama, Y.-T. Wu, A. Linden, K. K. Baldrige, J. S. Siegel, *J. Am. Chem. Soc.* **2007**, *129*, 12612-12613.
- [37] H. A. Wegner, L. T. Scott, A. de Meijere, *J. Org. Chem.* **2003**, *68*, 883-887.
- [38] Y.-T. Wu, T. Hayama, K. K. Baldrige, A. Linden, J. S. Siegel, *J. Am. Chem. Soc.* **2006**, *128*, 6870-6884.
- [39] a) E. A. Jackson, B. D. Steinberg, M. Bancu, A. Wakamiya, L. T. Scott, *J. Am. Chem. Soc.* **2007**, *129*, 484-485; b) B. D. Steinberg, E. A. Jackson, A. S. Filatov, A. Wakamiya, M. A. Petrukhina, L. T. Scott, *J. Am. Chem. Soc.* **2009**, *131*, 10537-10545.
- [40] A. Sygula, R. Sygula, P. W. Rabideau, *Org. Lett.* **2005**, *7*, 4999-5001.
- [41] A. Sygula, R. Sygula, L. Kobryn, *Org. Lett.* **2008**, *10*, 3927-3930.
- [42] a) Y. Himeshima, T. Sonoda, H. Kobayashi, *Chem. Lett.* **1983**, 1211-1214; b) Peña, D., Cobas, A., Pérez, D., Guitián, E. *Synthesis*, **2002**, 1454-1458.
- [43] L. Kobryn, W. P. Henry, F. R. Fronczek, R. Sygula, A. Sygula, *Tetrahedron Lett.* **2009**, *50*, 7124-7127.
- [44] R. N. Warren, *J. Am. Chem. Soc.*, **1971**, *93*, 2346-2348; R. A. Russell, D. E. Marsden, M. Sterns, R. N. Warren, *Aust. J. Chem.* **1981**, *34*, 1223-1234.
- [45] A. Sygula, R. Sygula, P. W. Rabideau, *Org. Lett.* **2006**, *8*, 5909-5911.
- [46] H. Becker, G. Javahery, S. Petrie, P.-C. Cheng, H. Schwarz, L. T. Scott, D. K. Bohme, *J. Am. Chem. Soc.* **1993**, *115*, 11636-11637.
- [47] S. Mizyed, P. E. Georghiou, M. Bancu, B. Cuadra, A. K. Rai, P. Cheng, L. T. Scott, *J. Am. Chem. Soc.* **2001**, *123*, 12770-12774.
- [48] T. Kawase, H. Kurata, *Chem. Rev.* **2006**, *106*, 5250-5273.

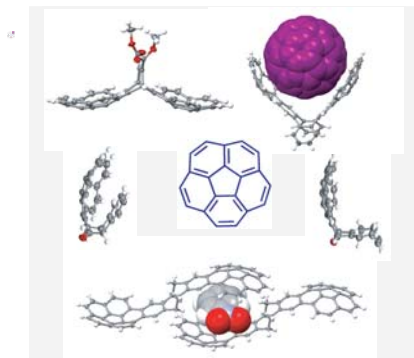
- [49] Y. Zhao, D. G. Truhlar, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2813-2818.
- [50] A. Sygula, R. Sygula, A. Ellern, P. W. Rabideau, *Org. Lett.* **2003**, *5*, 2595-2597.
- [51] A. Sygula, R. Sygula, P. W. Rabideau, *Tetrahedron Lett.* **2005**, 1189-1192.
- [52] A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau, M. M. Olmstead, *J. Am. Chem. Soc.* **2007**, *129*, 3842-3843.
- [53] C. Mück-Lichtenfeld, S. Grimme, L. Kobryn, A. Sygula, *Phys. Chem. Chem. Phys.* **2010**, *12*, 7091-7097.
- [54] F. R. Fronczek, A. Sygula, unpublished results.
- [55] a) B. M. Wong, *J. Comp. Chem.* **2009**, *30*, 51-56; b) A. A. Voityuk, M. Duran, *J. Phys. Chem. C* **2008**, *112*, 1672-1678; c) S. Chakrabarti, K. Ruud, *J. Phys. Chem. A* **2009**, *113*, 5485-5488; d) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104/1-154104/19.
- [56] W. Xiao, D. Passerone, P. Ruffieux, K. Ait-Mansour, O. Gröning, E. Tosatti, J. S. Siegel, R. Fasel, *J. Am. Chem. Soc.* **2008**, *130*, 4767-4771.

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Entry for the Table of Contents ((Please choose one layout.))

Layout 1:

Development of the practical preparations of buckybowls, bowl-shaped polycyclic aromatic hydrocarbons structurally related to fullerenes, is reviewed. Application of the recent methodologies allows for the construction of large carbon networks with corannulene subunit(s) exhibiting interesting properties and a potential for application as novel materials.



((Key Topic))

Andrzej Sygula

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