

Molecule of the Month.

Corannulene – A Bucky Bowl

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Surya Prakash Rao obtained his PhD from Indian Institute of Science. He is currently a Professor in Pondicherry University.

He has written an authoritative review with G Mehta on synthetic studies on fullerenes and fullerene fragments in "Advances in Strain in Organic Chemistry", Vol. 6, Ed. B. Halton, Jai Press, Greenwich, 1997. He seems to have found inspiration from, among other objects, the bowl-like structures of Pondicherry-Meeker houses.

The structure, properties and synthesis of a bowl shaped molecule, which resembles a fragment of fullerene, are described here.

Chemistry of aromatic molecules has a long history. Many molecules made up of multiple benzene-like rings have been isolated or made in the laboratory over the years. These are called polycondensed aromatic hydrocarbons (PAH for short). Being generally flat (and often carcinogenic!), most of these molecules have not attracted interest from a structural point of view¹. However, in recent times, some of these molecules have bounced back into the limelight due to the dramatic discovery of the third allotropic form of carbon, fullerenes. Closer examination of fullerenes reveals several interesting sub-structures. If these units are taken out and the valencies at the edge carbon atoms are saturated with hydrogen atoms, we would get curved molecules. Just as the fullerenes are affectionately called *bucky balls* by the practitioners in this area, non-planar fragments of fullerenes have been nicknamed *bucky bowls*. In this article, we feature one of the bowl-like units called corannulene (1).

During the late 1960s, W E Barth and R G Lawton conceived of a bowl like symmetric polycyclic aromatic hydrocarbon of the molecular formula $C_{20}H_{10}$ and called it corannulene 1 (*cora* is heart or within and *annula* is ring in Latin; IUPAC name is dibenzo[*ghi,mno*]fluoranthene). Almost 20 years after they first made this molecule, buckminsterfullerene or C_{60} (bucky ball), was discovered by a group led by R E Smalley, W H Kroto and R F Curl in the famous September 1985 experiments in Rice University, Houston, USA. Corannulene 1 fits into the surface of bucky ball and its siblings. In fact it forms both the cap and bottom of C_{60} and C_{70} .



It is evident from the structure of corannulene that the bond angle requirement of 120° for the peripheral benzene rings cannot be met if the molecule were to be flat. So, the molecule has considerable angle strain in the planar form. To avoid this, **1** assumes a bowl shape (*Figure 1*). The depth of the bowl has been measured by X-ray crystallography to be 0.87 \AA . It turns out that **1** is the smallest stable PAH to acquire a bowl shape.

As a consequence of its bowl shape, the aromatic resonance stabilization among the benzene rings is comparatively reduced. Corannulene can also be visualized as a novel type of aromatic structure with a 14π -electron rim and a 6π -electron core as shown in *Figure 1*. Both the 14 electron rim and the 6 electron core obey Huckel's rule of aromaticity ($4n + 2$ electrons). Therefore **1** can be treated as an annulene within an annulene.

Experimental evidence accumulated so far shows that **1** behaves like a regular aromatic compound. For example, it undergoes aromatic electrophilic substitution reactions (Friedel–Crafts) readily. Nuclear magnetic resonance (NMR) spectroscopic evidence (see *Box 1*) also points to the aromatic nature of the molecule (^1H NMR: δ 7.81 ppm, singlet; ^{13}C NMR: δ 135.8, 130.8 and 127.1 ppm).

Bowl shaped molecules can undergo an interesting dynamic process known as inversion². The bowl to bowl inversion is very fast in corannulene. It has been estimated that it inverts about

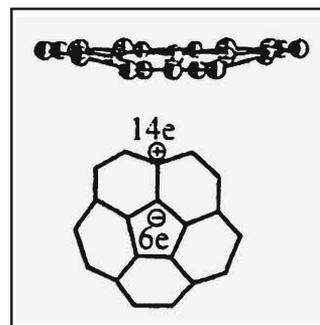


Figure 1. Bowl shape and anticipated resonance structure of corannulene **1**.

¹ Of course, there are exceptions. A sequence of six angularly fused benzene rings cannot remain perfectly planar because of steric repulsions. The molecule has to coil and adopt a helical shape. It has been named hexahelicene and was first made by Newman (also well known for the stereochemical representation named after him).

² For comparison, the inversion barrier in ammonia is only 6 kcal mol^{-1} .

Box 1

A signal around δ 7–8 ppm in the ^1H NMR spectrum indicates the aromatic nature of the organic compound. For example, benzene shows a peak at 7.28 ppm in its ^1H NMR spectrum. Similarly, peaks around δ 120–150 ppm in the ^{13}C NMR spectrum also indicate the aromatic nature of the molecule. Benzene shows a peak at δ 128.5 ppm in its ^{13}C NMR spectrum. One should note that the exact chemical shift (shift of the peak from the standard, tetramethylsilane, δ 0 ppm) depends on the solvent and the values given for corannulene and benzene are in deuterated chloroform.

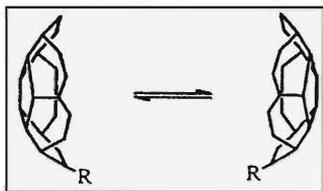


Figure 2. Bowl to bowl interconversion of corannulene derivative ($R=COH(CH_3)_2$).

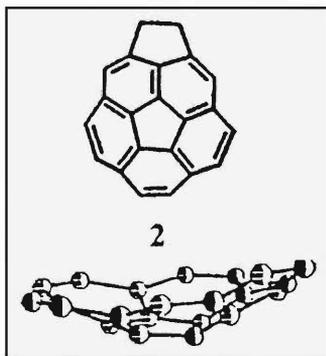


Figure 3. Cyclopentacorannulene 2 and its bowl structure.

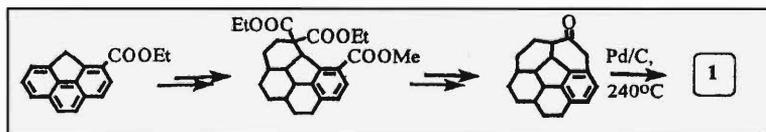
2×10^5 times a second. The energy barrier has been estimated to be about 10 kcal mol^{-1} in a derivative of **1** (Figure 2). However by joining one more cyclopentane ring on the corannulene structure, for example as in cyclopentacorannulene **2**, the inversion stops and the bowl gets arrested in a single conformation (Figure 3).

Corannulene and other bucky bowls have two distinct surfaces, *viz.*, concave (endohedral) and convex (exohedral). In the crystal, the bucky bowls can stack themselves in a concave to convex fashion, more like the arrangement of bowl-like utensils in a shop. On the other hand, concave to concave packing would look more like a sandwich. The X-ray crystal structure of **1** does not show any preferential packing and the molecules are arranged in several different relative orientations. However, cyclopentacorannulene **2** shows orderly concave to convex stacking in its crystal structure.

How is corannulene made in the laboratory? Almost three decades ago, Barth and Lawton achieved the synthesis of **1** starting from readily available 3-carbomethoxy-4*H*-cyclopenta [*def*]phenanthrene through 17 painstaking steps, which at that point of time was considered as a landmark in the synthetic chemistry of non-natural products. A brief version of their effort is shown in Scheme 1.

After the discovery of C_{60} , there has been renewed interest in the synthesis of corannulene and other bucky bowls. L T Scott and his group have synthesized **1** from commercially available acenaphthenequinone **3** in just three steps (Scheme 2). The synthesis reported in 1997 is an improvement over their original strategy published in 1991. The reaction sequence employs a highly imaginative fusion of a suitably substituted benzene ring to the quinone portion of the molecule (**3**→**4**), converting methylketone moieties to suitable derivatives (**4**→**5**) and finally

Scheme 1. Barth and Lawton's synthesis of Corannulene



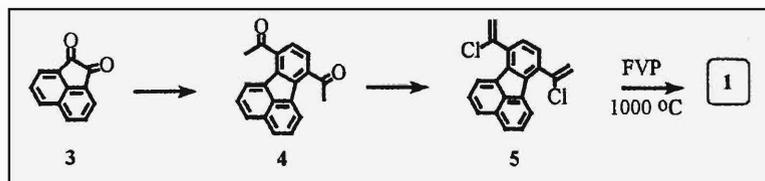
Box 2

The FVP technique employed in the penultimate step of Scott's synthesis is a well-known method for generating (or breaking) carbon-carbon bonds under high temperature conditions. In this technique, the vapor phase of the reactant is passed through a quartz tube (about 50 cm) pre-heated to high temperature (500°C–1300°C) under vacuum (10^{-4} –1 Torr). Since contact time with the hot zone is extremely small (about 10^{-6} sec), only the weakest bonds in the molecule break. Further, the required conformation of the molecule is generated for crucial carbon-carbon bond formation due to the high temperature used. This is important because the high energy conformations required for the generation of curved structures are generally not available under normal laboratory conditions. If contact times are large the whole molecule breaks up leading to charring. Thus, the success of FVP reactions is critically dependent on the applied temperature and vacuum.

employing flash-vacuum-pyrolysis (FVP, see *Box 2*) at 1000°C for double ring closure to furnish **1**.

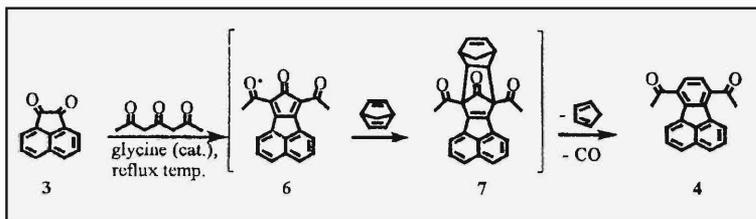
Conversion of quinone **3** to *bis*-methylketone **5** goes through several interesting transformations. Some details are provided in Scheme 3. The first step is the double Knoevenagel condensation to result in cyclopentadienone derivative **6** which is followed by Diels–Alder cycloaddition reaction with norbornadiene to furnish **7**. Under the reaction conditions retro-Diels–Alder reaction with the loss of cyclopentadiene moiety and retro-cheletropic reaction with the loss of carbon monoxide take place simultaneously to furnish benzoannulated product **4**. All these cascade reactions take place in a single pot and there is no need to isolate intermediates. In this transformation, norbornadiene acts as an acetylene equivalent and solvent.

Subsequent to Scott's original synthesis several research groups led by J S Sigel, G Zimmerman, P W Rabideau and G Mehta have also reported the synthesis of corannulene **1** employing FVP as the key penultimate reaction.



Scheme 2. Scott's synthesis of corannulene.

Scheme 3. Intermediates in the formation of diketone 4.



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Now that many procedures are available for making corannulene and other bucky bowls, more studies are expected on these interesting molecules. For example, the molecules may show differential metal complexation from the concave and convex surfaces. Some of the bucky bowls are chiral and have the potential to be employed as chiral catalysts in organic reactions. The future of bucky bowls is as bright as that of bucky balls.



J J Thomson of his own accord wrote a letter to his predecessor, Lord Rayleigh (a Nobel Laureate in 1904) about Sir J C Bose. The letter can be seen in the book entitled '*J J Thomson*', written by Lord Rayleigh's son, page 55, in the chapter, 'Early days of Cavendish Professorship'.

The letter starts as follows:

"The following refers to experiments on electric waves of Professor J C Bose".

November 16th, 1896

Dear Lord Rayleigh,

I have had occasion to read several of Bose's papers and am of opinion, that he is a very suitable person to receive 'Encouragement' if any is going. His experiments are ingenious, and his apparatus very well devised, and it must have required great patience and determination to make the apparatus work in a climate like that of India. The results are very interesting and his paper was received with great applause at Liverpool.

Yours truly,
J J Thomson