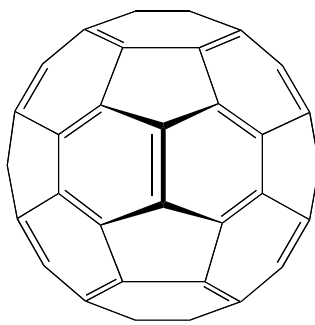


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PREMATURE DISCOVERY OF C₆₀**E. Ōsawa***NanoCarbon Research Institute, Ltd.*✉ osawa@nano-carbon.jp <https://orcid.org/0000-0002-1147-0898>**Introduction**

I am always amazed whenever I find seemingly simple rules prevail in nature. The structural principle of fullerene carbon is an example: network of any number of hexagons and exactly twelve pentagons forming a closed cage. Once this principle was understood, then so many structural variations were discovered one after the other including carbon nanotubes, carbon nanoparticles, and higher fullerenes in a short period of time, and now we recognize that fullerenes, namely the closed form of graphite having no edge, are of rather general occurrence[1].

No less amazing about fullerenes is that we did not know their existence only until recently, but they were there since ancient times, even before human being appeared on earth. Perhaps for this reason, people are curious if any scientist made notice of this ubiquitous form of carbon before the seminal discovery of C₆₀ (**1**), the masterpiece of fullerenes, by Kroto and others in 1985 [2]. As it turned out, several people had thought about C₆₀ molecule before them. For a notable example, I learned that Professor Schleyer once discussed the possibility of synthesizing this super-cage structure with Professor Chapman, who thereupon invested a few graduate students into this job. Unfortunately, the Chapman route did not work and they never published anything. This took place in 1980s [3]. Earlier, Drs. A. Stankevich and E. Gal'pern performed Hückel molecular orbital calculations of C₆₀ to obtain the now-well known characteristics of its frontier orbitals with five-fold degenerate HOMOs, and the three-fold degenerate LUMOs, the latter penetrating deep into bonding energy level, and published the results in a Russian journal [4].

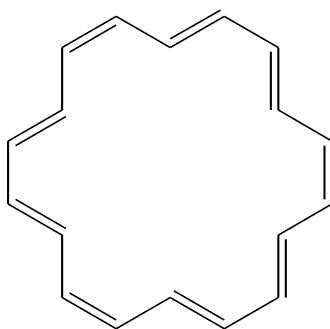
**1**

Chronologically speaking, I happened to be the first lucky guy. My youthful essay about the prediction on the possible electronic stability of soccer-ball molecule (as I called it at that time) was printed first in 1970 in a local chemical journal [5], then after revision in the following year as the last Chapter of my first book [6]. This book has long been out of print. These two publications can be hardly found in any library outside Japan because both of them are written in Japanese. Nevertheless, after fullerene research became popular, my 1970 journal article was cited more than 120 times as I found while checking Citation Index a few years ago. Apparently most of the authors quoted the work even without reading it. In order to respond to the intense interest in the first description of C₆₀ from so many people, I am writing this short article.

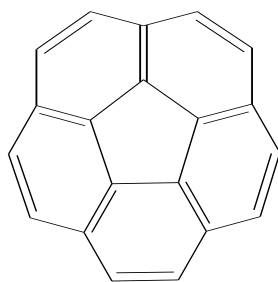
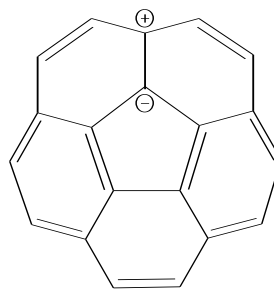
Attempted Extension of Aromaticity

Actually I mentioned about my premature discovery of C_{60} in some detail when I was invited to a Royal Society Meeting organized by Sir Kroto in 1992, and the content of the talk was published in the following year [7]. It would certainly be not appropriate to repeat the content here, but let me briefly reproduce its essence for Russian readers.

When I first thought of C_{60} , I had just come back home from 3 years of post-doctoral stint in the US and took up a post of assistant professor in Hokkaido University. Naturally I was looking for a new project to start my carrier as an independent reseacher. One of the popular topics at that time among organic chemists was the non-benzenoid aromaticity. Although I liked the expansion of the old but vague concept of aromaticity to a wider structural framework with the theoretical prediction by Hückel as the guiding principle, I was too late. The beautiful work of Franz Sondheimer on annulenes, especially the magnificent molecule of [18]annulene (**2**), soared so high before me like Mt Everest that all subsequent works in this field seemed like an imitation of his style [8]. How can I circumvent the disadvantage of a late comer? After some thoughts I came across an idea of enlarging the dimension. It seemed that no one ever attempted to escape from the dogma of delocalizing conjugated π -electron system over a planar molecule. Why not three-dimensional delocalization which should give much higher aromatic stabilization?

**2**

The key molecule I had in mind at that point was corannulene (**3**). I knew about this molecule since one of the evening seminars of Professor Schleyer's group in Princeton took it up soon after the synthesis by Barth and Lawton in 1968. Interests in the seminar centered around its unknown structure: there were two possibilities, double-looped planar non-benzenoid aromatic (**4**, inside 4π , outside 14π , both aromatic), and tub-shaped benzenoid. After coming back to Japan, I read the result of X-ray analysis of corannulene single crystal by Lawton [9]. To my surprise, it was a shallow tub, apparently a compromise between the non-benzenoid and benzenoid aromatics. It still took sometime before I could connect the corannulene structure with 3D aromaticity. One day as I was watching my small son playing with a soccer ball, I suddenly saw that soccer ball had the structure of corannulene. Closer look revealed that corannulene constitutes its basic pattern, nicely overlapped with each other to cover spheroidal surface. Instantly I saw that this is an ideal model of 3D-aromaticity! I soon learned that the geometry of soccer ball is one of the Archimedean non-regular solids called truncated icosahedron.

**3****4**

Afterthoughts

The following are the results of my recent analysis on the reason why I stopped to work on C₆₀. For the following few days since I noticed the possibility of constructing a molecule having the geometry of truncated icosahedron from sixty sp²-hybridized carbon atoms, I enjoyed thinking of the molecular ball, but then finally I decided to abandon, a decision later proved to be the greatest mistake I have ever made in my life. The reasons of my abandoning C₆₀ are as follows. First I thought about the possibility of building up C₆₀ step by step by the method of organic synthesis, but it soon became clear that this molecule was too difficult. I was not good at the art of organic synthesis, anyway. I was then concerned about many benzene rings in C₆₀. The known molecular structure of corannulene retaining planar benzene rings seemed to me to indicate the dominance of the aromaticity of benzene, a masterpiece of all aromatic molecules. Typical non-benzenoid aromatic molecules like [18]annulene and cyclopropenium tactfully avoid the inclusion of hexagons, which may disturb extensive delocalization of π -electrons but confine the conjugative delocalization within hexagons.

My memory of C₆₀ was still clear when I saw the *Nature* paper [2] 15 years later that reported the first observation of C₆₀. Evidence of structure the authors presented in that paper was weak, but I wished to believe that this is an experimental proof of the superaromaticity I had in mind. Then I became uneasy to realize that C₆₀ was formed *spontaneously* during laser ablation of graphite and annealing in helium thereafter. Indeed, if C₆₀ were truly 3D-aromatic and exceptionally stable, the wisest way to make it must be to let carbon atoms work themselves to form the stable structure spontaneously. Why did I fail to recognize this natural route to obtain C₆₀? Obviously the formation of such a large cage structure is accompanied by a large loss of entropy, hence must be thermodynamically very unfavorable process. Continued failure in the total synthesis of C₆₀ even now attests to this thermodynamic principle. It is now clear that the secret of success by Kroto and others is the use of extremely high temperatures in their experiments, which must have compensated the entropic disadvantage to turn the free energy of formation of C₆₀ to a negative value.

Thus, I understood that my task of designing the preparation of C₆₀ in 1970 was a very hard one. Chemists generally do not think of temperatures like 20,000 K (temperature at the site of laser ablation), but our maximum reachable temperature is that of flash vacuum pyrolysis, about 1300 K, above which all organic compounds decompose. This was a mental pitfall that appears when an organic chemist thinks of the one-step preparation of entropically unfavorable molecule. There is another reason why we need high temperature to form C₆₀. On the basis of recent computational-theoretical studies, we know that the crucial step to achieve the symmetric pattern of C₆₀, in which all the pentagons are isolated and surrounded only by hexagons, is believed to be an energetically very expensive step called Stone-Wales rearrangement [10].

What about the danger of destructive decomposition of C₆₀ at temperatures higher than 1300 K? How C₆₀ molecules survive in temperatures of several thousand K after they are formed? Actually C₆₀ molecules survived in the experiments of Kroto *et al.*, because, in my opinion, two key factors acted favorably and effectively to avoid thermal decomposition. These factors are rapid cooling and closed structure. At very high temperatures, the fullerene-forming reactions are complete in a split of a second, therefore extremely rapid cooling can be applied, and was actually applied in their experiment. The second factor, closed structure of C₆₀ (or in general fullerenes), precludes large vibrational modes. C₆₀ has only four very weak vibrational frequencies in the infrared, thus the initial steps of thermal decomposition are strongly suppressed. Hence, all the conditions for C₆₀ formation were miraculously satisfied in their experiments.

At this point, I am again impressed to see another manifestation of very simple principle controlling the formation process of fullerenes. The new principle is the 'rigid cage structure'. One of the advantages of having a structure without edge is the absence of dangling bonds. This is well known since Kroto and his coworkers used this idea to propose the closed structure for C₆₀. However, another advantage of the rigid cage has never been well recognized before, which is to protect the molecule from decomposing by suppressing the seed of decomposition, the thermal vibration, as mentioned above.

Final words

In retrospect, if I were to continue the work on C₆₀ in 1970, I had to have enough imagination and drive to foresee and solve all those problems as mentioned above. This task was clearly too hard, and it almost seems natural that I abandoned the project at that time. The bitter oversights notwithstanding, however, I still feel myself as very lucky. I am rejoiced by the fact that a dream came true while I am still alive. I even participated in its research and watched my brainchild growing up quickly to eventually become probably the best studied of all the known molecules in the history of science: more than 20,000 papers on C₆₀ have been published by now. All three awardees of 1996 Nobel Prize for Chemistry generously referred my 1970 article at the beginning of their Nobel lectures [11]. At the moment, industrial applications of fullerene carbons are imminent and it is truly exciting to imagine myself watching flat-panel display of a wall TV illuminated by electron beam from carbon nanotubes in not too distant future. I am thankful to the lucky star under which I was born.

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