PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Evolution of the Football Structure for the C $_{60}$ Molecule: A Retrospective [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1993 **343**, 1-8
doi: 10.1098/rsta.1993.0035

The evolution of the football structure for the C_{60} molecule: a retrospective

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By chance in 1970, we conjectured the possibility of the football-shaped C_{60} molecule, now known as buckminsterfullerene, while considering superaromatic molecules having three-dimensional π-electron delocalization. A translation of the original description, initially written in Japanese, is given. The processes leading to scientific discoveries are analysed in the light of our missed opportunity.

1. Introduction

The timescale of scientific and technological advance is becoming shorter and shorter in modern society, partly as a consequence of the rapid advance of technology and improving information transfer. It is no wonder then that the time has come to look back and discuss the future of fullerene science after less than a decade since its discovery by Kroto *et al.* (1985) and after only two years since it was isolated by Krätchmer *et al.* (1990). The purpose of this paper is to recount the story of original early proposal of the football-shaped C_{60} molecule back in 1970, and refer to other interesting 'prehistoric' events and analyse the process of scientific discovery.

2. Background

In the 1960s and 1970s, non-benzenoid aromatics were favourite targets for organic chemists. There was a prevailing dogma that aromaticity, due to the delocalization of π-electrons, is best realized in planar molecules. Everyone wished to constrain their molecules to be as planar as possible and for this reason aromaticity tacitly remained a two-dimensional concept. [18]Annulene (**1**), synthesized by Sondheimer *et al.* (1962), can be regarded as the masterpiece of planar aromaticity for its symmetric beauty (D_{6h}) and high level of π-electron delocalization. In view of the wide availability and its perfect aromaticity, however, benzene remains the archetypal superstar of aromatic molecules.

Our goal in those days was to find a new π-system more aromatic than king benzene. Then came the news of the corannulene (**6**) synthesis by Barth & Lawton (1966) and its bowl-shaped structure quickly aroused strong interest among us. As is mentioned below, analysis of its structure logically led us to conceive the extrapolation of its structure to a sphere so that we could envisage three-dimensional delocalization of the π-electrons. Fortuitously about that time my small son started

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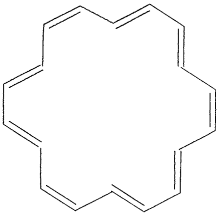
to play with a football and the pattern of the corannulene molecule was immediately and clearly recognizable in it. Careful study of the design of the ball soon led to the recognition that it was a truncated icosahedron.

The I_h-symmetric C_{60} molecule was first described by Ōsawa (1970), and the concept expanded the following year in the final chapter of Yoshida & Ōsawa (1971). The book was read widely by Japanese chemists. There was, however, little response to my proposal of the potential stability of the football-shaped molecule. In the meantime, for reasons mentioned below, we stopped working on aromaticity and engaged in new fields of research until the classic paper of Kroto *et al.* (1985) appeared. In 1986, O'Brien, then a graduate student with Smalley at Rice University, U.S.A., asked Yoshida for an English copy of this book and we produced a translation of pertinent portions (pp. 174–178) for him. This translation (slightly polished) is reproduced below.

3. Possibilities of superaromatic hydrocarbons

We temporarily define the term 'superaromaticity' as the lowering of energy that might occur when electrons delocalize over molecular orbitals on the surface of some three-dimensional surface of high symmetry. Is there any possibility of ever realizing such a phenomenon with hydrocarbons?

Let us take a look at the back cover of Cram and Hammond's *Textbook of organic chemistry*, where a number of 'dream molecules' are depicted. Truncated tetrahedrane, or heptacyclo[$5.5.0.0^{2,12}.0^{3,5}.0^{4,10}.0^{6,8}.0^{9,11}$]dodecane, $C_{12}H_{12}$ (**2**) appears to offer a possibility of its cyclopropane bonds with high p-character to interact over the surface of the molecule. Structure **2** has eight faces and is formally obtained by truncating four vertices of tetrahedron (**3**): it is also the target of synthesis by several research groups (Woodward 1970).



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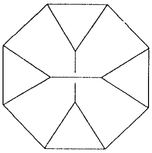

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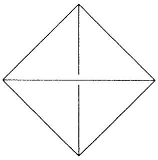

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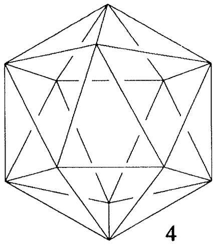
Another possibility of realizing three-dimensional (3D) aromaticity would be to consider electron delocalization, not among σ orbitals on the sphere, but through p_z orbitals directed perpendicular to the surface of sphere. If such conjugation is to be achieved over the surface of spheroidal skeleton composed of carbon atoms, then the sphere will have to be large, so that the p_z–p_z overlap is not reduced too much compared with that for a planar skeleton. If we follow the strategy of truncating a Platonic solid to produce a near-spheroidal structure, as mentioned above, the icosahedron (**4**) seems to provide a large enough skeleton for our purpose.

Truncation of a vertex of this solid produces a regular pentagon at that place and truncation of all twelve vertices gives a beautiful 32-faced solid, which is called the truncated icosahedron (**5**). The solid has the same design as that appearing on the surface of an official modern football. Study the ball yourself. Among the pentagons, hexagons are buried in a highly symmetric manner. The component polygons do not seem to be deformed very much from their planar form, and all the 90 edges have almost the same length. Then, the C_{60} molecule which results from replacing 60 vertices by sp^2-hybridized carbon atoms does not seem totally unrealistic.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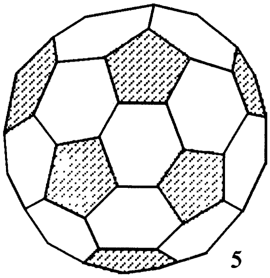
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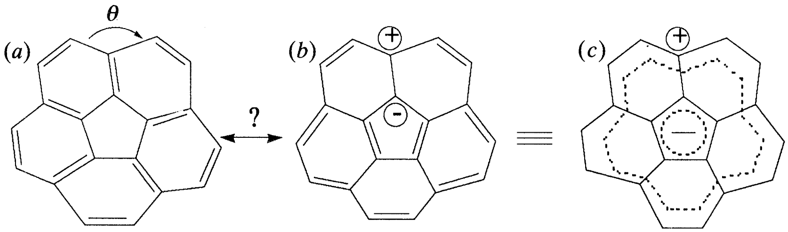
Interestingly enough, Barth & Lawton (1966, 1971) recently synthesized a molecule that corresponds to a part of the surface design of the football: dibenzo[ghi,mno]fluoranthene (**6**) with a five-membered ring surrounded by five six-membered ring. This hydrocarbon gives almost colourless, stable prismatic crystals melting at 268–269 °C and is named corannulene. According to X-ray analysis, the molecule is bowl-shaped (**7**) and indeed appears to correspond to a segment of structure **5**.



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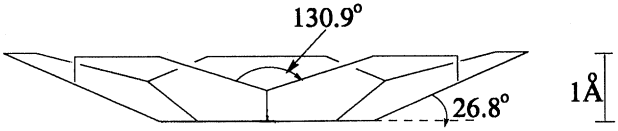

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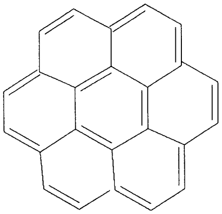
It should be noted, however, that planarity had not been excluded for corannulene until the X-ray analysis was performed. The molecule is a non-alternant hydrocarbon because it contains an odd-membered ring. Hence, the π-electron density distribution cannot be uniform in the ground state. One of such polar structures is the double Hückel aromatic structure **6***b*, *c* consisting of peripheral 14π and central 6π systems. The contribution of resonance as shown in **6***c* will be at its maximum when the whole molecule is planar like coronene (**8**). Notwithstanding, the planar corannulene will have huge angle strain. If we assume that all C–C bonds are 1.40 Å in length and the central ring is regular pentagon for the planar corannulene, then the angle θ shown in **6***a* will be as large as 144°. Out-of-plane deformation of five bonds extending from the pentagon may release some of the angle strain. The deformation would be, however, as large as 38° if the standard value of 120° is to be restored for θ (**9**). Then the neighbouring benzene rings would no longer be coplanar and the stabilization energy, by delocalizing the π-electrons, would be greatly reduced.



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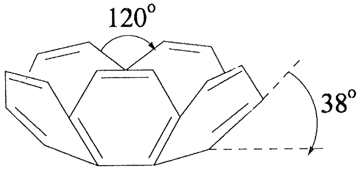

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At this point, we notice that the corannulene molecule provides an ideal model for addressing a very interesting problem: how much aromaticity is lost when a molecule is distorted from the strongly aromatic planar structure to a nonplanar structure? The answer to this question must be a key to the possible existence of *superaromaticity* in the C_{60} molecule (**5**).

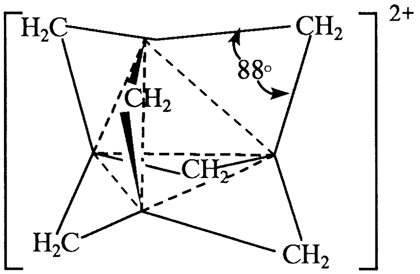
Let us look again at the X-ray structure of corannulene (**7**). The observed angle between the pentagon and the hexagons is 26.8° in average. Therefore, considerable strain must remain in the skeleton. The observed angle θ between the six-membered rings is 130.9°. The actual structure of the corannulene molecule is a shallow bowl (**7**) somewhere between the planar structure (**6**) and the deep-bowl form (**9**). The NMR chemical shift (2.19 τ) suggests considerable aromaticity. It is reported that this molecule forms weakly coloured charge-transfer complexes with picric acid and trinitrobenzene (Barth & Lawton 1971).

It is still not clear how much of the resonance energy that would have been obtained in the planar form is lost in the shallow-bowl structure. According to SCF–LCAO–MO calculations by Gleicher (1967), even the deep-bowl structure (**9**) retains more than 90% of the π-bonding energy that can be realized in the planar form, and the resonance energy amounts to at least 10 kcal mol^{-1}.

4. Discussion

Having reproduced our old proposal, the outcome is now briefly described. According to Aihara's (1988) topological theory of aromaticity, the resonance energy per π electron (REPE) of **5** is calculated to be 0.0274 β, or about 60% of that of benzene (0.0454 β). It is thus clear that there is no dramatic increase in the conjugative stability in **5**. As far as aromatic stabilization in the football structure is concerned it should be regarded as an extension of two-dimensional aromaticity. Aihara & Hosoya (1988) call it spherical aromaticity.

A true example of 3D delocalization, and consequent stabilization, was later discovered by Schleyer (1987) and described in his award lecture. The superaromatic organic molecule that he presented is a 2π system contained in a tetrahedral space within the adamantane skeleton (**10**). However, how can one create a superaromatic system with more than two electrons? This problem still remains a challenge to chemists.



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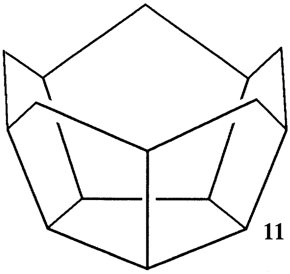
It is noteworthy that about the same time as our book was published, two Russian chemists performed Hückel molecular orbital calculation on C_{60} (Bochvar & Galpern 1973). They named it carbo-s-icosahedrene. Their calculations gave the correct picture of the π-orbital system.

It may be of some interest to us to trace how the structure **5** occurred in the minds of these authors. According to their paper, the impetus came from Eaton's (1972) work on the synthesis of peristyrene (**11**), a potential precursor of dodecahedrane, $C_{20}H_{20}$ (**12**). Noting that the C–C–C and C–C–H angles in **12** are expected to be very close to the tetrahedral value, they scanned through the five regular Platonic polyhedrons and 14 semiregular archimedean polyhedrons for similar situations. They found the truncated icosahedron of particular interest, because the carbon atoms in the hydrocarbon analogue ($C_{60}H_{60}$) or carbon analogue (C_{60}) of this polyhedron 'can be considered to be very near to an sp^2-hybridized state'. They thought of dodecahedrane (**12**) and C_{60} (**5**) as the strainless polyhedral molecules consisting exclusively of sp^3- and sp^2-carbon atoms respectively.



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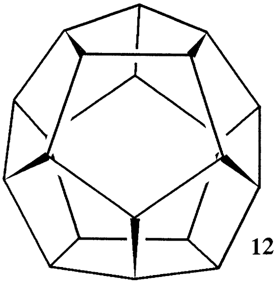

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The two preliminary studies of **5**, ours and that of Bochvar and Galpern, have different starting points – corannulene and dodecahedrane – but have one thing in common: both parties did not pursue then imaginary molecule any further. Why is it that these early concepts did not develop logically into substantial studies? Perhaps neither of us recognized the hidden potential of the football structure of C_{60} as a new form of carbon and if so we should be categorized as *premature* discoverers, according to Stent (1972, see also Landman 1992).

At least in our own case, however, there were three distinct reasons for not pursuing this problem, and it seems worthwhile to record them here. First, at a time when there was absolutely no anticipation for the possibility that the football structure might form spontaneously, we thought it almost impossible to realize the synthesis of **5**. This fear proved correct: we recently learned that Chapman's arduous attempts to the synthesis in the 1980s were never rewarded (Diederich 1992).

The second reason might sound rather surprising: we actually thought this molecule not particularly interesting (Ōsawa 1991). There are several grounds for this conclusion. As mentioned above, there was no response to our original proposal and we were very discouraged. Furthermore, **5** contains as many as 20 'benzene' rings. Although these rings are deformed out-of-plane, the case of corannulene has taught us that the six-membered rings will tend to remain planar and this should be a source of its stability. Hence, it seemed likely that the stability as well as all other properties of football C_{60} will be very heavily influenced by the presence of so many 'benzenoid' units. Actually, this concern existed from the inception of the football structure. We therefore wished to devise a totally new molecular system of superaromaticity as it would clearly be desirable to have something quite different from the 'benzene analogue'.

The third reason for our premature rejection of **5** was, as has recently been correctly guessed by Karfunkel (1992), the underdeveloped status of computational chemistry in those days: computers large enough to handle C_{60} were not available to us. Even when we performed the first semiempirical MO calculations of C_{60} and C_{70} in 1986, the molecules were rather too large to be studied by routine calculation and we had to work half a year debugging the program until we finally succeeded in detailed vibrational analysis (Slanina *et al.* 1987*a*,*b*, 1989; Rudzinski 1987).

5. Final words

No scientific discovery seems to be totally new, as has been discussed superbly well by Berson (1992) with reference to the discoveries of the Diels–Alder reaction and the Woodward–Hoffmann rule. In the case of C_{60}, the 'near misses' by Iijima (1987) and the unpublished work by Chapman (Diederich 1992), are more pre-eminent examples of the precedence than those described above.

Let us conclude our presentation by a comment on the relative importance between the well-known two steps in the process of discovery: finding and the recognition of finding (Berson 1992). Our inevitable conclusion, after observing such a large number of missed discoveries, is that the latter is much more important and difficult than the former. A finding is usually made by chance, as in the case of the discovery of the C_{60} peak in the mass spectrum of laser-vaporized carbon clusters (Kroto *et al.* 1985). Hence there is not much one can do but to resort to serendipity.

The most crucial moment comes after a finding has been made. The most desirable situation would be that the discoverers themselves recognize the relevance of their finding and explain the relations with the then accepted body of knowledge, using a language that leads others to logically understand the significance of the discoveries. Here a number of novel qualities are required: the imagination to grasp generality on the basis of a small piece of evidence, the talent to give an appropriate name (Nickon & Silversmith 1987) and the ability to communicate well with other scientists. It is truly gratifying to realize that the authors of the 1985 *Nature* paper had all these attributes.

We thank Dr R. N. Compton for a copy of English translation of the Bochvar & Galpern paper.

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Discussion

H. W. Kroto (*University of Sussex, U.K.*). The Hückel rule is $4n+2$. Does this apply to three-dimensional aromaticity? Patrick Fowler has his $6k+60$ rule for C_{60}, but are there different rules for different structures?

P. W. Fowler (*University of Exeter, U.K.*). The only closed shells in fullerenes are those that obey the $6k+60$ rule, and another series that obeys the $30k+70$ rule. If you want closed shells you will not get one, electronically, below C_{60}. So the question of whether C_{60} is aromatic is another story. I think the chemistry is showing that C_{60} is anything but aromatic, and the serendipity was trying to think of an aromatic system, finding one, and then realizing that it wasn't.

E. Wasserman (*Du Pont Experimental Station, U.S.A.*). The word aromatic has so many different meanings, it is very hard to use it in any brief sense, with any degree of accuracy. Certainly, some of the things that we and others have found, on debromination, chlorination and dechlorination of C_{60}, indicates a ready reversion to C_{60}. In planar systems we would regard that as partial evidence for aromaticity. The fact that there are other forms of aromaticity simply means that we are beginning to stretch the term a little far.

P. W. Fowler. You can make a case for the aromaticity of C_{60}. We have called it a molecule of ambiguous aromatic character, because it is clear that it does not follow all of the rules, particularly those set by benzene. When most chemists talk of aromaticity, they probably compare the molecule to benzene as this is the only perfect aromatic compound that we have and it sets a pretty high standard. Consider other compounds that chemists traditionally consider as aromatic, for example, the next highest Hückel molecule, 10-annulene. If we look at the chemistry that has been done on the bridge 10-annulenes, much of it does not follow closely the standards set by benzene. The fact that most derivatives of C_{60} tend to revert to type does make a case for the aromaticity of C_{60}. There are many counter examples, and one is the question of ring currents in C_{60}, which do not appear as simple as in other aromatic compounds. So I do agree that it does not follow all of the rules. Adding to the example that you gave of corannulene (**6**) in which the five-membered ring at the centre of the molecule has six π-electrons, and the outer perimeter had 14 π-electrons, Harry Scott has just succeeded, with Mordicai Rabinowitz, in adding four electrons to corannulene. You now have six electrons in the centre of the molecule, and 18 electrons on the periphery. In that way it can be imagined as an aromatic outer 18 π-electron system, and an inner six π-electron system, which nicely confirms the things you were talking about.

E. Ōsawa. I have something to add on the tendency of chlorine and bromine derivatives of C_{60} to revert to C_{60}. One of the reasons for this tendency is not only aromaticity, but also the strange properties of the σ-bonds extending outside the structure. These σ-electrons have π-electrons as neighbours; a unique situation in organic chemistry. As a result of σ/π interactions, the σ-bond will be very weak, so this could be one of the reasons for the reversal of halogenation.