

Fully Arenoid Toroidal Fullerenes, both Benzenoid and Non-Benzenoid.

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ABSTRACT

The concept of polycyclic systems that are fully arenoid (that is, that can be represented as a set of identical, smaller arene systems connected by single bonds) is briefly examined in the context of toroidal fullerenes. The lack of a perimeter allows for additional subtleties of structure when compared with their bounded, finite and topologically-planar counterparts.

INTRODUCTION

Originally it was Armit and Robinson¹ who pointed out the importance of the aromatic sextet as a determinant of the properties that have come to be known as 'aromatic', and, later, Clar and Zander²⁻⁴ who noticed that benzenoid structures seem to show greater stability when they can be drawn as a set of self contained benzene rings connected by single bonds. Such benzenoid structures, referred to here as being *fully* benzenoid (fig.1) have attracted a fair amount of attention,⁵⁻¹⁵ although they form a rather small subset of all possible benzenoids.¹⁶

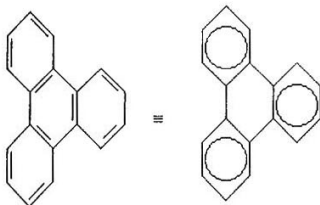


Figure 1. Triphenylene, a fully benzenoid structure.

A fairly obvious development, parallel to the Hückel extension of the aromatic sextet to ' $4n+2$ ' systems in general, is to consider structures that can be considered as singly connected assemblies of larger aromatic systems. Obvious or not, however, little work was done on such systems until quite recently,^{11,17-22} but fully naphthalenoid planar systems have now been

characterised.¹⁷ There is no reason either, to confine our attention to the all-hexagonal benzenoid systems. Azulenes have been the most studied of polycyclic non-benzenoid hydrocarbons²³ and were probably the first to be described as at least partially aromatic. In many reaction conditions azulene has a propensity to form stable ionic species by electron abstraction from the seven membered ring. Fully-azulenoid structures, especially those of infinite or unbounded size might therefore have interesting properties. Another related and particularly interesting class of hypothetical closed structures is based upon azulene-1-yl methene units (Figure 9, Appendix II), but these are hydrocarbons, not fullerenes and are outside the scope of this paper.

This special journal issue attests to the importance of and interest in fullerenes, and it is reasonable to ask whether fully-arenoid fullerenes could be as important as their planar counterparts. The famous and archetypal fullerene structure buckminsterfullerene is not fully arenoid in the quite the same sense, but on the other hand it is 2-factorable (see definitions below) into a set of pentagons, and can be viewed as being a polyhex structure with pentagonal 'holes'. Other spherical C_{60} and higher isomers are not considered further here, where attention is confined to the *toroidal* fullerenes. Toroidal species are of interest for the reason, among others, that, being of genus-one, they can in principle be constructed entirely of hexagons,²⁴ and thus are directly comparable with finite planar benzenoids. In this short paper we briefly discuss both benzenoids and azulene as possible arenoid units within C_{60} toroidal isomers. We restrict the review to this size because demonstration of the principles, and comparison with buckminsterfullerene, is more convenient. It is well known that in practice, because of geometric strain, only larger structures ($\approx C_{150}$ and above) are likely to be realisable as stable physical objects.²⁵

At this point a mild controversy surrounding the concept of 'fully arenoid' should be mentioned. The original definition introduced by Clar and Zander² allowed as fully-arenoid any structure that *can* be drawn as an assembly of arenes connected by single bonds, not just those structures that *must* be drawn in this way. Knop et al.¹² have argued that this stricter definition only (a special case of the former) should be used, leading to the conclusion that benzene is the *only* fully-benzenoid benzenoid-system. In this paper, however, we retain the broader definition embracing systems that *may be but need not be* essentially singly connected. A justification for the continued usefulness of this has been advanced by Gutman and Cyvin.¹⁹

DEFINITIONS AND NOMENCLATURE

We use the unqualified term **fullerene** to denote any cubic graph of genus-zero. This means that it is graph-theoretically planar and like buckminsterfullerene can be embedded on the surface of a sphere, but, in contrast to some workers, we make no stipulation about ring sizes. We further allow, by qualification and obvious extension, the notion of **toroidal-fullerenes** or

Klein bottle-fullerenes and so on. For the particular case where the notional toroidal surface has only hexagonal faces, we frequently use the term **toroidal polyhex**.²⁴

Here we use the term **fully arenoid** in the sense already described above, but a further stipulation must be made for these non-planar tori: Because a structure of this type has a boundless surface, it has additional circuits present that curve through the third dimension around the torus, and which, subject to the effectiveness of π -orbital overlap, may be stabilizing ($4n + 2$) or destabilizing ($4n$). Such 'non-facial' rings are excluded in this treatment. The surface rings that are included within the arenoid units are called **full** rings, while the others that remain are said to be **empty**. Other sometimes more restricted but overlapping terms in use include **fully acenoid**,¹⁸ **perfect Clar**,²⁶ **total resonant sextet**,^{5,9} **2-factorable**,¹⁶ **sextet-2-factorable** and **n-circuit 2-factorable**.²¹ A fully acenoid (catacondensed benzenoid) structure is necessarily 2-factorable. A fully arenoid benzenoid system in general will be 2-factorable if the arenoid is catacondensed (i.e. is an acenoid), but if it is pericondensed *and not* 2-factorable, then the possible 2-factorability of the whole system remains an open question as far as we know. (A **2-factorable** graph is one that can be overlaid with a set of disjoint circuits, and every vertex accounted for.)

FULLY ARENOID TOROIDAL POLYHEXES

Fully benzenoid species are amenable to a fairly simple characterisation based on a three-integer code used to identify the toroidal polyhex itself (See Appendix I). Being fully benzenoid depends upon the first integer and the sum of the remaining pair of integers both being divisible by three; details were given in an earlier paper.²¹ Of 141 toroidal polyhex isomers with 12-60 vertices, 27 are sextet 2-factorable or fully benzenoid, and four of these occur among the 13 toroidal C_{60} isomers. (Note that Table I of reference²¹ contains a misprint, for in one case the wrong C_{60} structure is marked as fully benzenoid, although this is obvious when the above rule is applied.) Other fully arenoid toroidal polyhexes are less straightforward to characterize. We have not yet given attention to this and merely report observed fully naphthalenoid structures in Table I. Over a sample of moderately sized structures fewer fully naphthalenoid than fully benzenoid structures were found, but this appears to be due more to the fact that fewer numbers (of vertices) are divisible by ten than are divisible by six, rather than a significantly smaller proportion of multiple-ten systems being fully naphthalenoid. Features of interest about the fully benzenoid toroidal polyhexes include the facts that

1. Fully benzenoid toroidal polyhexes cannot be fully benzenoid in the restricted sense used by Knop et al.¹² - i.e. there are no essentially single bonds. In this respect they are no different from finite planar benzenoids, always excepting benzene.
2. The full and the empty sets of hexagons are not unique. Since the surface of such a polyhex

is unbounded, any single hexagon is indistinguishable from any other, and any hexagon may be defined as 'full' - although once it is so defined, the categorisation of all others as full or empty is fixed. This fact suggests that characterisation as fully benzenoid may have less significance for toroidal than for the planar species examined by Clar, especially since it is associated with the presence of zero eigenvalues (non-bonding orbitals) and a zero (Hückel) HOMO-LUMO gap. On the other hand the phenomenon *enhances* the resemblance of these toroidal structures to graphite, for an infinite graphite sheet also has this interchangeability of rings.

3. A planar benzenoid system cannot be both fully benzenoid and fully naphthalenoid at the same time, but this is not true of toroidal structures, as fig.2 and Table 1 show. There are other possible combinations too. Among toroidal polyhexes with 28 and 56 vertices for example (not shown here) are three that are both fully anthracenoid and fully phenanthrenoid. It will be interesting as more work is done to see whether being multiply-fully-arenoid is merely an intriguing curiosity or whether it reflects anything deeper.

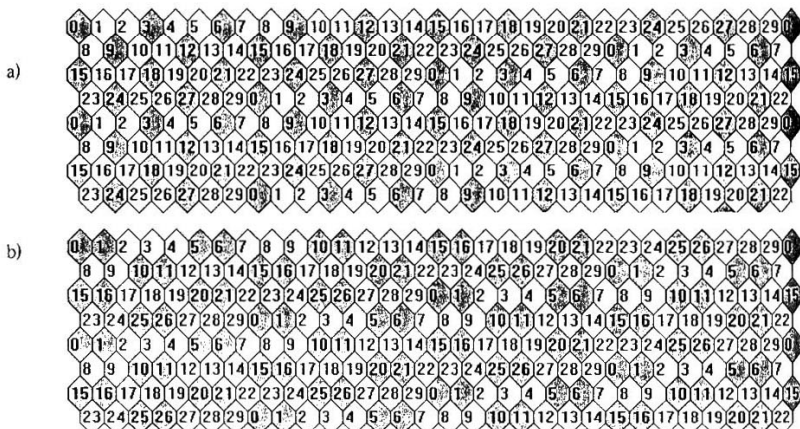


Figure 2. Toroidal polyhex 30-8-1 shown as (a) fully benzenoid and (b) fully naphthalenoid.

Toroidal Polyhex	Fully			E_{π}	GAP	
	Benzenoid/	Naphthalenoid/	R_{30} ?			
TPH 15-05-2	-	-	-	94.7318	0.8316	30-0-30
TPH 30-02-1	yes	yes	-	85.9175	0	28-4-28
TPH 30-03-1	-	yes	-	95.9905	1.2360	30-0-30
TPH 30-04-1	-	-	-	94.5534	1.1762	30-0-30
TPH 30-05-1	yes	-	-	93.5188	0	28-4-28
TPH 30-06-1	-	-	-	94.5496	0.8316	30-0-30
TPH 30-07-1	-	yes	-	94.5185	1.0056	30-0-30
TPH 30-08-1	yes	yes	-	92.9229	0	28-4-28
TPH 30-09-1	-	yes	-	94.4192	0.7640	30-0-30
TPH 30-10-1	-	-	-	93.6107	0.4182	30-0-30
TPH 30-11-1	yes	-	-	93.0511	0	28-4-28
TPH 30-12-1	-	yes	-	94.3811	0.7640	30-0-30
TPH 30-15-1	-	-	yes	93.8127	2	30-0-30
Buckminsterfullerene				93.1685	0.7560	30-0-30

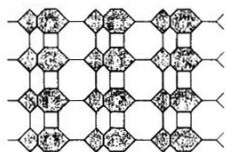
Table 1. *C₆₀ toroidal polyhexes examined for being fully arenoid with respect to linear acenes with 6, 10 and 30 vertices (the only '4n+2' factors of 60), together with their Hückel energies, HOMO-LUMO gap and numbers of positive, zero and negative eigenvalues.*

FULLY AZULENOID TOROIDAL FULLERENES

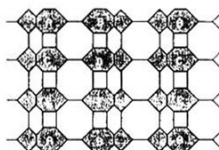
The taxonomy of what can be described as *azulenoid* fullerene structures is considerably more complicated than is the case for polyhexes, and these have by no means been fully classified. One group of structures, briefly considered in an earlier paper²⁷ has a lattice that contains *only* the five- and seven-membered ring pairs of the azulene system, but such networks do not appear to be amenable to the localisation of individual azulene ring systems necessary to be *fully* azulenoid.

There is however another class which, although less 'pure' in the sense of having a wider range of face sizes, can nevertheless be easily formulated as fully azulenoid. Here the empty set contains rings of other sizes with six, and sometimes four and eight vertices. Such a possibility does not arise with fully arenoid benzenoids. These are exemplified by Table II which shows 14 fully azulenoid isomers that derived from the 3 x 2 'azulene rectangle'

(fig. 3). This square is to be imagined folded over so that opposite sides join and thus form a torus strung with bracelets of azulene units. As the bracelets are rotated around the tube relative to one another up to 360° (breaking and remaking connections), fresh connectional isomers are formed. For benzenoids, the high symmetry attending such a process means that more isomorphisms and fewer distinct isomers occur, and generally, only rotation of one band up to 180° will be productive. (The purely *geometric* twisting isomerism that is unrelated to connectivity is of course being ignored here.) Additional isomers can be generated by not restricting 'horizontal' bonding to be all head to tail; compare figure 3 with 4 for example.



E_x 90.2616



E_x 90.2610

Figure 3. 'All head to tail.'

Figure 4. Figure 3 'head to head'.

An additional, but related, novelty of these systems when compared with benzenoids is that ring size distributions will vary in a periodic manner with these rotations. Imagine two azulene bracelets sliding past each other; the interleaving band - which is part of the empty ring set since the whole is fully azulenoid - goes through a -4-8-6- to a -5-6-7- to a -6-7-5-repeating sequence (counting from the bottom of a 7-ring), suggesting a greater difference of physical properties should they ever be physically realised.

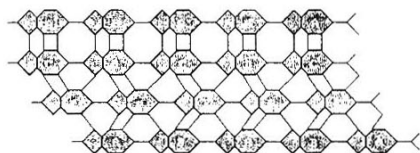


Figure 5. The fully azulenoid toroidal fullerene (3) after twisting successive bands by an increasing amount.

It was pointed out above that for fully arenoid toroidal polyhexes, the full and empty ring sets are not unique, whereas they are in the case of finite planar structures. Here, for azulenoids, both conditions can occur. In figure 3 only one set of azulene units is available for the full set, but in figures 6 and 7 there are two possibilities in each case.

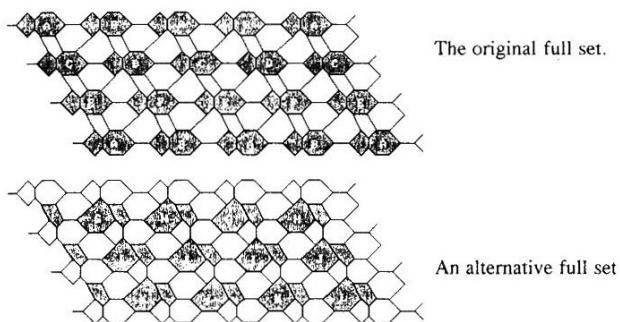


Figure 6. *The fully azulenoid of figure 3 with each bracelet twisted one position.*

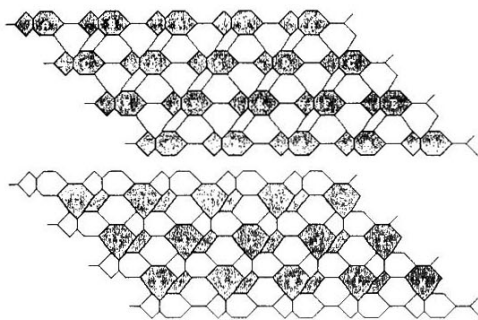


Figure 7. *Fully azulenoid (fig.3) with each bracelet twisted two positions. This also is fully azulenoid in two senses.*

Twist Code ^a	E_{π}	GAP	
000	90.2616	0	29-2-29
001	90.6719	0.1116	30-1-29
002	90.6585	0.0088	29-1-30
003	90.0465	0.1787	30-2-28
011	91.4974	0.0216	31-0-29
012	91.4995	0.1414	31-0-29
021	91.0656	0.0416	30-1-29
041	91.1985	0.0777	30-0-30
042	91.2425	0.1020	30-0-30
051	91.2674	0.0416	30-1-29
111	92.2388	0.3369	30-0-30
112	92.0177	0.2011	30-2-28
114	92.2099	0.3539	30-0-30
115	92.3926	0.5494	30-0-30

Table II. Fourteen Fully Azulenoid C_{60} isomers together with their Hückel energies, HOMO-LUMO gap and numbers of positive, zero and negative eigenvalues.

^aThis is an informal code used to distinguish isomers of (3) obtained by cyclic permutations of the connections between horizontal rows of azulene units. Each digit represents the number of shifts in one row. Note that this is not a full enumeration of isomers. A search for isospectral partners involving $T(G)$ matrices²⁸ has not been undertaken, and neither have all possible twists and azulene reversal modes been examined.

CONCLUSION

Fully arenoid toroidal fullerenes are *not* directly comparable with their planar counterparts, and the likely magnitude of any stabilizing effect is uncertain. Observations on physical structures probably to be realised in the future will be awaited with interest.

APPENDIX I: The encoding of toroidal polyhexes.

We use a three-digit code which was described in detail, together with its application for adjacency matrix compilation and eigenspectrum evaluation, by Kirby, Mallion and Pollak.²⁴ The graphical basis for this has been shown²¹ and is summarised here. It provides a simple qualitative recipe for using the code.

The toroidal polyhex is drawn as part of an infinite hexagon lattice, on which one (arbitrary) 'origin' hexagon is marked wherever it occurs on the repeating pattern of the toroidal surface. The size of section taken is not important so long as it is large enough to see the full pattern. The rectangle enclosed by four such marked hexagons defines the connectivity on the toroidal surface, and the rectangle can itself be defined by two pairs of Cartesian coordinates, chosen so that one coordinate out of the four is zero. A unique value for the array ($a-b-d$) is chosen by minimising first d , then b , when there is a choice of rectangles that could be used. Figure 8 shows an example.

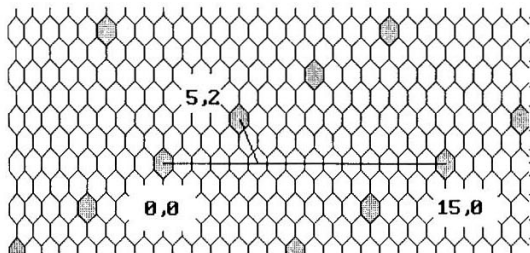


Figure 8. The encoding of Toroidal Polyhex 15-5-2. (Codes 6-3-5 and 6-2-5, among others, are equivalent but are rejected by the ordering rules used).

APPENDIX II.

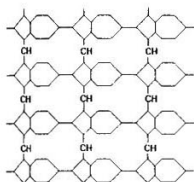


Figure 9. The skeleton of an interesting but non-fullerenic azulene-based network for forming closed structures

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