communications in mathematical
match
and in computer chemistry

no. 48, February 2003
MATCDY (48) 179- 188 (2003)

ISSN 0340 - 6253

THE DISPOSITION OF NON-HEXAGONAL RINGS AROUND NANOTUBE T-JUNCTIONS

Edward C. Kirby

Resource Use Institute 14 Lower Oakfield, Pitlochry, Perthshire PH16 5DS, Scotland UK

ABSTRACT. Open-ended carbon nanotubes, like toroidal fullerenes, can and probably do exist as fully hexagonal, graphite-like structures, but if two tubes are joined by cutting a hole in the wall of one and joining it to the end of another, this is no longer possible, and inevitably there will be at least two non-hexagonal rings. Here we explore some of the smaller and simpler constructions using both graph theory and molecular mechanics to see the extent of their deviations from graphitic objects, and suggest a possible way of encoding them. T-junctions made from tubes with six hexagons round the circumference and with sides parallel to their cylinder axes, could all be optimised into a plausible geometric representation.

INTRODUCTION

A nanotube is a cylinder of carbon atoms, normally arranged in a polyhex structure, and in concept may be viewed as a rectangular sheet of graphite which has been rolled up, and one pair of opposite sides glued seamlessly together. Thus, only at the ends of the cylinder are there degree-2 vertices (or, equivalently, carbon atoms having a pendent hydrogen atom available for substitution); all internal vertices are of degree 3, corresponding to trigonally hybridised carbon atoms. These objects, together with fullerenes of varying topology, have been the subject of much research in recent years [1-5], and one of their possible uses for the future is as a new class of electrical conductors. They are plausible candidates for components of what eventually might become the near ultimate 'molecular-sized' computers. For any complex circuitry, networks of tubes, and therefore junctions, may be needed. There have been a number of studies of nanotube junctions although most are concerned with the end-to-end joining of two nanotubes in order to tailor the geometric or electrical properties of a single 'wire'. The practical preparation of junctions of three tubes in a "T" or "Y" shape appears to be difficult, but it has been done. [6] Here it is not immediately obvious what is structurally possible even from a theoretical point of view, and it is this question we explore here. A practical chemist in need of a tubular glass T-piece, and not having one to hand, might take two lengths of glass tubing, heat the side of one, blow a hole in it, and then fuse its rim to one end of the other tube (see Figure 1.). In essence this is the process we have modelled here. There is a problem, however. While the chemist, by careful annealing of the artefact can make a T-Piece junction where the glass wall has exactly the same physical properties anywhere on its surface, this is not the case for these nanotubes made from networks. The surface of a straight nanotube is well suited to a graphite-like, all hexagon structure, but a T-Junction necessarily has some non-hexagonal rings where a tube end joins a larger hole. The structure networks we deal with here are entirely hexagonal except for this annulus of rings that forms the collar where the two tubes join. In this paper we do not attempt any extensive enumeration, but we discuss the variables, and show a few examples.

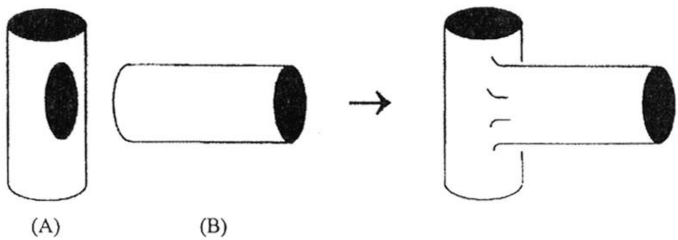


FIGURE 1. Schematic view of T-Junction construction from two Cylinders: A, having a hole in its side, and B.

STRUCTURAL FEATURES

The characterization of these species can be considered from two viewpoints. For fully comprehensive knowledge of course, all connectional information is needed, and so the dimensions of the tubes must be known: the orientation of the hexagons; how the tubes are joined together to form a T-Junction; whether the T-Junction is open ended or part of some larger structure, and so on. For many purposes, however, we need to concentrate on the purely local features of the junction, and to consider features common to any particular environment. This is the main objective here, so that topologically we are concerned simply with joining a cylindrical network to a hole in a hexagon lattice. Although object A in Figure 1 is shown as a cylinder, and this is used for the examples constructed, it could equally well be any other polyhex network such as a torus, a graphite sheet (some pictures of these have been published [7]), or an all-hexagon region of a conventional spherical fullerene.

The annulus

This circular band of rings that connects the surface of one of the original cylinders to that of the other, is where all the non-hexagonal rings occur in the class of structures considered here. Some, but not all, of these may be hexagons, and clearly the distribution of rings and their sizes depend on the nature of both the cycle that forms the end of one cylinder, and the cycle that forms the boundary of the side-hole in the other cylinder.

The junction components that by interconnection form the annulus

In the simplest case the cylinder whose end is joined to the hole (cylinder B in Figure 1), is one whose hexagons are aligned so that each has two sides parallel to the axis (referred to as 'anthracene type'), and whose ends are 'cut square' with no protruding hexagons. This has alternating degree-2 and degree-3 vertices around each end. If the hexagon alignment is rotated by 90 degrees to become perpendicular to the cylinder axis (referred to as 'phenanthrene type'), then the pattern of degree-2 and degree-3 vertices is different, but the ratio and the total numbers are unchanged. For other shapes, where there are protruding or missing hexagons, both the numbers and sequence patterns of the vertices may change but, nevertheless, the degree-2: degree-3 ratio stays the same (see Theorem 1). For the purpose of making a T-Junction, the number of degree-2 vertices must, obviously, match that of the hole. In the simplest case of an anthracene type cylinder with a minimum length boundary at the end, rotation of the cylinder relative to the hole has no effect. In all other cases the effect of such rotation must be checked for possible generation of new non-degenerate structures.

Because the boundary cycle at a cylinder end need not be at its minimum (i.e. the end may not have a 'straight cut'), the circumference, measured in hexagons, is only loosely related to the number of free degree-2 vertices, and in any case, within wide limits the cylinder sizes are not required to match. It is the side-hole of one and the end of the other that must be compatible, and the circumference of cylinder B, whose end is attached (Figure 1) can be much greater than that of cylinder A if the hole in A is narrow, slit-like and aligned diagonally or along the axis.

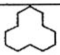
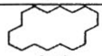
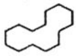
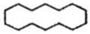
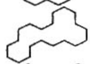
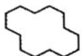
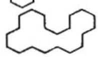
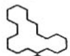
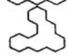
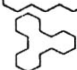
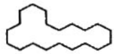
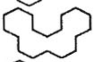
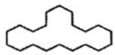
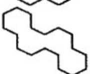
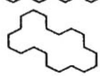
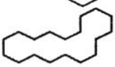
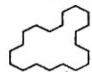
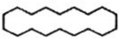
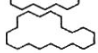
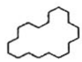
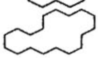
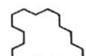
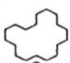
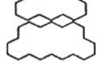
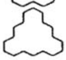
A benzenoid cylinder with a hole (A in Figure 1) can be viewed simply as a once-folded & glued coronoid whose outer boundary is rectangular. Both benzenoids[8, 9] and coronoids[10] are quite well characterized objects. To illustrate a few examples we have used the systematic tables given by Knop et al.,[11] who list smaller benzenoids using a three-integer code *h.i.j* where *h* is the number of hexagons, *i* the number of internal vertices and *j* is a sequential reference number generated by their algorithm. By identifying benzenoid patches on the cylinder side, and then deleting vertices and edges internal to the patch, one may generate coronoid holes systematically; Table I shows some examples, and each will generate a different isomer. If the hole (see Figure 1A) lacks full rotational symmetry, then its orientation relative to Cylinder B is important. Orientation of the hole can also vary with respect to the axis of Cylinder A, and the possibilities are of course affected by whether Cylinder A is of anthracene- or phenanthrene-type. The position of the hole on cylinder A needs to be specified too. If Cylinder A is closed to a torus then neither position nor orientation of the second type (hole on A relative to axis of A) has connectional significance, although the ease of physical realisation may vary.

CONSTRUCTION

A useful property of the annulus that contains non-hexagonal rings, somewhat reminiscent of the Euler closure rule for polygons, is that its size deviations from six, sum to six, and a proof is given below.

Theorem 1: When the degree 2 vertices at one end of a cylindrical polyhex, are joined to those around the inner boundary of a suitably sized coronoid, by connecting degree 2 vertices

Table I. Coronoid holes formed from polyhexes with up to seven hexagons, to which a polyhex cylinder can be attached. A: The number of attachment points (degree 2 vertices), c, required; B: solutions for h,i (=hexagons, internal vertices) of the equation $2h$-2-i = c that exist as distinct coronoid holes; C: reference codes of the corresponding polyhexes; D: the shapes of the holes, i.e. the polyhexes of column C with their internal vertices and incident edges deleted.

A	B	C	D	A	B	C	D
3	3,1	3.1.1		6	6,4	6.4.3	
4	3,0	3.0.1		6	7,6	7.6.1	
4	3,0	3.0.2		7	5,1	5.1.1	
4	4,2	4.2.1		7	5,1	5.1.2	
5	5,3	5,3,1		7	5,1	5.1.3	
5	4,1	4.1.1		7	5,1	5.1.4	
6	4,0	4.0.1		7	5,1	5.1.5	
6	4,0	4.0.2		7	5,1	5.1.6	
6	4,0	4.0.3		7	6,3	6.3.1	
6	4,0	4-0-4		7	6,3	6.3.2	
6	4,0	4-0-5		7	6,3	6.3.3	
6	5,2	5.2.1		7	6,3	6.3.4	
6	5,2	5.2.2		7	7,5	7.5.1	
6	5,2	5.2.3		7	7,5	7.5.2	
6	6,4	6.4.1		7	7,5	7.5.3	
6	6,4	6.4.2		7	8,7	8.7.1	

one-to-one from each, then for the annulus of new rings formed, the sum of the deviations from six of each ring size itself equates to six, i.e.

$\sum$ (Annulus ring size-6) = 6 (1)

Proof: Consider some benzenoid B and a benzenoid patch B* within it. The size and shape of B is immaterial provided B* is entirely surrounded by hexagons. For B* let h be the number of hexagons, v the number of peripheral vertices, and v_3 the number of vertices of degree 3. The number of these on the perimeter of B* will be v_3-i where i is the number of internal vertices. These peripheral vertices of degree 3 become those of degree 2 (v_2) within the coronoid hole formed by deletion from B of the i vertices and their incident edges that are internal to B*.

v_2 (coronoid) = v_3-i (benzenoid) = $2h$-2-i (2)

v (coronoid) = v (benzenoid) = $4h$+2-2i (3)

These results are given by Cyvin et al[10], and are implicit in Gutman et al.[8]

We consider now the cylinder that is to be connected to the hole, and first take the special case of the anthracene type where the all the degree 2 vertices at one end lie on a plane perpendicular to the axis. There will be v_2 degree 2 vertices (by definition) plus an equal number of degree 3 vertices evenly interspersed, i.e. the vertex degree sequence around the cylinder end will be 2,3,2,3,2,3.... With the alternative arrangement for the hexagons (phenanthrene type) the degree sequence is 2,3,3,2,2,3,3,2,2... Again there are equal numbers of degree 2 and degree 3. Finally there is the case where the degree 2 vertices are not all in a plane perpendicular to the axis, because the cylinder end has protruding or missing hexagons. Figure 2 shows all the addition modes for adding hexagons to a polyhex, which indicates that although the number of degree 2 vertices for a given cylinder varies with the shape of the end, the ratio of degree 2 to degree 3 vertices does not. It follows that

v (cylinder) = $2v_2$ (4)

Now the total boundary of the annulus will be formed by all vertices around the coronoid hole ($4h$+2-2i) plus all vertices around the end of the polyhex cylinder ($2v_2$), but of this total, v_2 pairs of vertices are shared between two rings. It follows that

$\sum$ (Annulus ring size) = 4h+2-2i + $4v_2$ = $4h$+2-2i+ 4($2h$-2-i) = $12h$-6-6i. (5)

The ring size sum for an annulus with the same number of hexagons is

6 v_2 = 6($2h$-2-i) = $12h$-12 –6i, and the result follows.

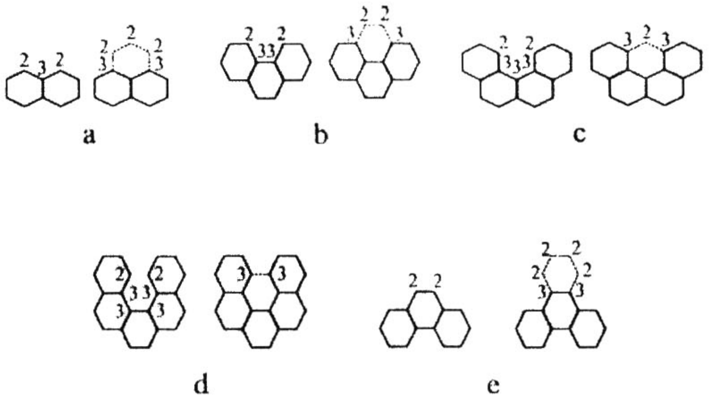


FIGURE 2. Modes for adding one hexagon to a polyhex. The effects on the numbers of degree 2 and degree 3 vertices (v_2 and v_3) are to (a) a fissure: + 1,+1 (b) a bay: no change (c) a cove:-1,-1 (d) a fjord: -2,-2 (e) a promontory, +2,+2.

It should be noted that Theorem 1 provides a simple numerical check on the sizes of additional rings or faces formed. It does not imply that all ring patterns from a given cylinder are the same; they are not.

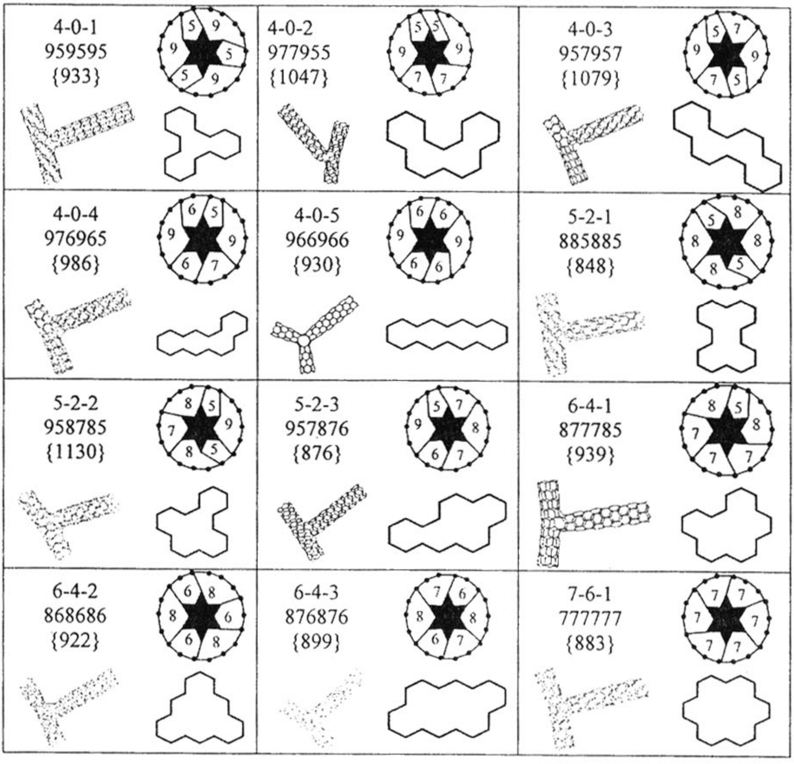
As an example, junctions derived from 6-hexagon circumference cylinders of anthracene type were constructed. Table 1 shows that there are twelve coronoid holes that meet the requirement of six degree 2 vertices on the inner boundary, and the use of these when joined to 'square-cut' cylinders of the same type is shown in Table 2. All the examples were constructed using HyperChem [12] and could be optimised to a plausible geometry using HyperChem's molecular mechanics geometry optimisation facility, although in many cases, unless the starting geometry was chosen carefully, the final structure settled into an unrealistic and locally non-planar structure. The ease with which a nice structure could be obtained appeared to bear no relation to the hole shape and resultant ring pattern. For reliability it was found best to conduct the optimisation in stages - i.e. to construct and optimise the two cylinders, then assemble them with the hole and a cylinder end in reasonable spatial proximity, connect them, and finally, re-optimise the whole.

In so far as such models give any guide to physical reality, it is noteworthy that although there were slight variations, most structures did optimise as "T" rather than "Y" structures. The exceptions were junctions made from the hole 4-0-2, where the concerted effect of two pairs each of 9, 7 and 5-membered rings bends and narrows one of the tubes, and the simple polyacene hole 4-0-5. In this case an even "Y" structure forms, whose only deviation from all-hexagon coverage is two nine-membered rings lying either side of the junction in planes parallel to the three tubular arms. In general it can be expected that geometry will vary even less with larger structures, as non-hexagons become a smaller part of the whole. Further studies are in progress.

THE ENCODING OF T-JUNCTIONS

In the preceding section it was shown that a simple maximized clockwise circular string of ring sizes contained within the annulus, together with a code for the coronoid hole, suffices to encode a junction where the joined cylinder is of anthracene type, and has a minimal boundary at the connected end. To encompass other types of cylinder however – phenanthrene type or those that have a non-minimal boundary – more information is needed. A suggested more general form of the code uses ring sizes in the same way, but intersperses them with the numbers of vertices that are of degree 3 on the cylinder end (or, equivalently, are degree 2 on the inner perimeter of the annulus). Thus, for example, the code for a junction from a simple anthracene type with the 4-0-5 hole, shown in Table 2 as 966966, becomes 9-1-6-1-6-1-9-1-6-1-6-1, showing that each ring of the annulus contains one degree 3 vertex on the inner side. In Table 2 this amounts to scoring one for each of the indentations of the inner star. More complicated arrangements can now be dealt with. For example a simple phenanthrene type cylinder, instead of the vertex degree sequence (2,3,2,3,2,3...), has (2,2,3,3,2,2...) on its ends. Using this with hole 4-0-5 would give the code 10-2-5-0-7-2-8-0-7-2-5-0, and again there is only one isomer here because of the symmetry of both components, but if we join the same cylinder to the hole 4-0-4, two distinct isomers may be obtained: 10-2-6-0-7-2-8-0-7-2-4-0 and 10-2-5-0-6-2-8-0-8-2-5-0. More complicated cylinder ends may be dealt with by similar means. If required, the circumference of cylinder B, its type and its end shape can all be reconstructed from these code values. So also, although somewhat more laboriously, can the original hole in cylinder A. The lengths, however, remain unspecified

Table 2. T-Junction construction from polyhex tubing of six hexagons circumference with each hexagon having two sides parallel to the axis (anthracene type). The cylinders used are all 12 hexagons deep. For each example is shown, clockwise from upper left: (i) the code[11] for the polyhex used to generate a hole, a string of the annulus ring sizes generated (as the highest clockwise lexicographic value) and in parentheses the minimized energy after molecular mechanics optimisation; (ii) the annulus formed by attaching the cylinder end (represented by a six point star) to the hole; (iii) the shape of the corresponding polyhex hole before attachment, and (iv), an image of the result generated by HyperChem [12]



CONCLUSIONS

A T-junction made from polyhex tubes must contain at least two non-hexagonal rings. In the class of structure considered here, where all deviations from hexagonality occur within the annulus formed when a polyhex tube is joined to a hole in the surface of another polyhex tube the tubes join, the deviations sum to six, providing a useful computational check. The local structure of such a junction can conveniently be characterized as a maximized string of annulus ring sizes interspersed with the numbers of degree 3 vertices on the attached cylinder end. Additionally, a code for the hole is helpful but not essential. A set of twelve junctions that require six connections between the tubes all gave pictures showing a plausible geometry under a molecular mechanics optimisation.

REFERENCES

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162.

[2] P. C. Ecklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, London, **1996**.

[3] *The Science & Technology of Carbon Nanotubes*, Elsevier, Kidlington , Oxford, **1999**.

[4] P. J. F. Harris, *Carbon nanotubes and related structures: New material for the twenty-first century*, Cambridge University Press, **1999**.

[5] D. Tomanek, R. J. Enbody,eds. *Science & Applications of Nanotubes: Proceedings of nanotube conference 24-27 June 1999, East Lansing, Michigan, USA.*,Fundamental Materials Research ed. M. F. Thorpe,**1999**, Kluwer.

[6] J. Li, C. Papadopoulos, J. Xu, *Nature* **1999**, *402*, 253 .

[7] E. C. Kirby, T. Pisanski, *Journal of Mathematical Chemistry* **1998**, *23*, 151.

[8] I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag, Berlin Heidelberg New York, **1989**.

[9] G. Caporossi, P. Hansen, *Journal of Chemical Information and Computer Sciences* **1998**, *38*, 610.

[10] S. J. Cyvin, J. Brunvoll, B. N. Cyvin, *Theory of Coronoid Hydrocarbons, Vol. 54*, Springer Verlag, **1991**.

[11] J. V. Knop, W. R. Müller, K. Szymanski, N. Trinajstic, *Computer Generation of Certain Classes of Molecules*, SKTH/Kemija u industriji, Zagreb, **1985**.

[12] *HyperChem, version 6.03*, Hypercube, Inc., Gainsville, Florida, USA.