Mat. Res. Soc. Symp. Proc. Vol. 675 © 2001 Materials Research Society

# Designability of Graphitic Cones

**M. M. J. Treacy and J. Kilian**
NEC Research Institute, Inc. 4 Independence Way, Princeton, NJ 08540-6685, USA

## ABSTRACT

We show that, with topologically flexible seeds which are allowed to explore different growth modes, graphitic cones are inherently more "designable" than flat graphitic disks. The designability of a structure is the number of seed topologies encoding that structure.

We illustrate designability with a simple model, where graphite grows onto $C_n$ ($5 \le n \le 30$) ring seeds. For a wide range of ring sizes, cones are the most likely topological outcome. Results from the model agree well with data from special cone-rich carbon black samples.

The concept of designability allows entropy to be incorporated into the "pentagon road" model of the formation of curved graphitic structures.

## INTRODUCTION

Recently, Krishnan et al. (1997) [1] reported a new carbon black material, made by Kvaerner Engineering a.s. Norway in a proprietary industrial process that involved the pyrolysis of methane in a plasma torch. Transmission electron microscopy (TEM) showed that the sample (designated KVR) contained high concentrations of multilayer graphitic disks, cones and tubes. Cones had been sighted before in carbon black [2], but not in the quantity and variety exhibited by KVR. Five distinct cone angles were observed, each corresponding to the inclusion of a disclination of order $1 \le m \le 5$. The measured cone angles, $\theta$, were found to correspond closely to the predicted values $\theta = 2\sin^{-1}(1 - m/6)$. Although graphitic disks dominated the sample, among the cones the medium-angle 60° ($m$=3) and 38.9° ($m$=4) cones occurred most frequently.

From an energetics viewpoint, the small-angled cones (those with the sharpest cone points and largest $m$ value) should have the highest elastic strain energy per carbon atom, particularly near the tip area where cone wall curvature is high. Furthermore, there is an additional energy penalty for forming the tip structure, which must enclose one or more disclinations. Although pentagon inclusion probably costs the least energy on forming the core of the disclination, defect structures with dangling bonds and different ring sizes are also possible. From consideration of the enthalpy of formation alone, the disk topology with no strain and no pentagons, must be the lowest energy form, and the 19.2° ($m$=5) cone and the cylinder ($m$=6) must be the highest energy forms, and therefore the rarest. An enthalpy argument would predict, in terms of $\theta$ values, the order of likelihood to be $180° > 112.9° > 83.6° > 60° > 38.9° > 19.2° > 0°$. TEM shows, however, that the 180° disks, and the 60° and 38.9° cones dominate the KVR sample.

The reason must lie with the differences in Gibb's free energy, $\Delta G_{ij} = \Delta H_{ij} - T\Delta S_{ij}$. As usual, $\Delta H_{ij}$ is the enthalpy of formation when a chemical system transforms from state $i$ to state $j$, and $T$ is the temperature at which the transformation occurs. The entropy change $\Delta S_{ij}$ is a measure of the number of reaction pathways available to system $i$ that can lead to product $j$. If a chemical system $i$ is inundated with opportunities to form a higher enthalpy product $j$, then entropy can dominate the rate of product formation.

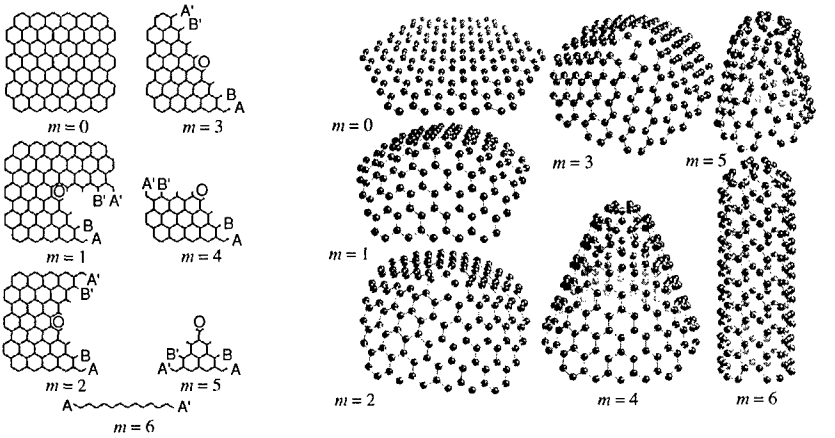


**Figure 1:** Illustration showing how to construct the five cones and a cylinder from a hexagonal graphite sheet. Multiples of 60° segments are systematically removed, and dangling bonds are re-connected. Each cone can be characterized by the number $m$ of 60°segments that are removed. $m$ is also known as the disclination number. $m$=1,2,3,4,5 correspond to true cones. The $m$=0 planar sheet, and the $m$=6 cylinder are considered here to be end-members of the family of cones.

In this paper we present in more detail an entropy argument, first outlined in Krishnan *et al.* (1997) [1], that explains the observed cone distribution. For simplicity, we focus the discussion on monocyclic hydrocarbon rings as model nuclei for graphitic growth. We count the number of ways in which a carbon $C_n$ ring can be embedded into a conical structure so as to circumscribe the cone tip. This count is the "designability" of the structure [3]. We show that $C_n$ rings ($n \geq 5$, $n \neq 6$) encode conical graphitic structures more prolifically than they do planar graphitic sheets. With topologically flexible seeds, cones are highly designable relative to planar graphite.

## STRUCTURE OF GRAPHITE CONES

To date, there have been several theoretical papers discussing cone topologies [4, 5]. The conical shape arises naturally when 60° segments are cut out of a planar graphite sheet, and the severed edges of the segment are rejoined. A maximum of six 60° segments can be removed. Figure 1 shows how this process works. The removal of one to five 60° segments, followed by the physical connection of reference points A to A', and B to B', results in five distinct types of cone, the tips of which are girdled by a continuous curved hexagonal framework. Topologically, the removal of six 60° segments does not necessarily lead to the removal of all atoms; it is equivalent to a chain of atoms, which when connected end to end, produce a ring. The stacking of identical rings generates a cylinder. The cylinder and disk are the topological end-members of a seven-membered family of cones. The removal (or addition) of 60° segments in a planar lattice introduces defects known as *disclinations*. Cone topologies are differentiated by referring to the number of 60° segments that are removed. This is the disclination number $m$. For all carbon atoms to be 3-connected, cone tips must incorporate ring sizes other than 6-rings. Such rings introduce curvature into a framework, resulting in rounded cone tips. Pentagons can be sufficiently isolated so that, locally, each pentagon appears to be a part of an $m$=1 (112.9°) cone. Pentagons cannot be arbitrarily close to each other. The *isolated pentagon rule* (or IPR), which applies to structures formed entirely from 5- and 6-rings, stipulates that each pentagon must be

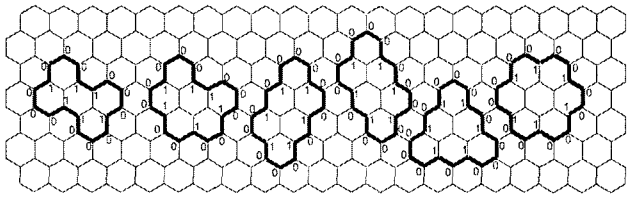


**Figure 2**: The six topologically distinct open-ring $C_{18}$ circuits that occur in $m$=0 graphite. They can be represented by cyclic binary sequences, with 1 representing a bond "inwards" and 0 a bond "outwards". (c) and (d) are mirror images. There are 18 cyclic permutations of each ring type, giving a total of 108 permutations. Cross-linked modes are excluded in this example.

completely surrounded by hexagons. This rule can be justified by simple chemical arguments – the extent of $sp^3$ re-hybridization (in other words, the non-coplanarity of the central atom with its three bonds) must be minimized at each carbon atom.

Pentagons are generally considered to be the preferred "defect" ring size in hexagonal $sp^2$-hybridized networks, as evidenced by their abundance in the Fullerenes. The disclination parameter $m$ is then equal to the number of pentagons required to form the cone tip.

## CARBON *n*-RING MODES

Consider a closed $C_{18}$ circuit in a graphite sheet. Six distinct open-ring topologies are possible (Fig. 2), presenting a total of 6×18=108 cyclic configurations. A convenient method of describing these circuits in planar graphite is to label the one free bond at each carbon that extends from the ring. An outward-facing bond is assigned the label "0", and an inward-facing bond the label "1". These sequences can be permuted cyclically, anti-cyclically or mirrored without changing the topology (except for the handedness – for example Figs 2c and 2d).

Upon removing these 18-carbon circuits from their graphite matrix, the "1" and "0" bonds become dangling bonds and are free to move. In fact, the ring is free to change shape. Chemically, such a ring is free to adopt one of a huge number of distinct chemical structures based on permutations of single, double or triple bonds. We ignore such distinctions, since topologically the rings are identical once they are embedded in graphite. For a cone or cylinder, the distinction between a "0" and a "1" becomes clear by executing a clockwise path along the circuit, beginning at any atom. An atom is assigned "0" when the sense of the bond rotation *in the ring* is clockwise, and "1" when the rotation is counterclockwise.

The rules for growing a closed annulus of graphite onto the perimeter of a carbon ring (or circuit) are easily derived. For planar graphite formation, the outer circuit of the graphitic annulus contains 12 additional atoms. In general, for a disclination of order $m$, the relationship between the size $n_k$ of the inner, and size $n_{k+1}$ of the outer, circuits of the graphitic annulus is $n_{k+1}-n_k=12-2m$. The number of inward-pointing bonds $i_k$ is related to the number of outward-pointing bonds $o_k$ by $o_k - i_k = 6 - m$, with $n_k = o_k + i_k$. There are $2^n$ binary representations of a $C_n$ ring. This number is greatly reduced by the constraints on $o_k - i_k$. By examining the binary form of all integers between 0 and $2^n-1$, $m$-values can be obtained from $m=6+i_k-o_k$. A further constraint is that atoms may not collide, disallowing modes with more than five consecutive 1's or 0's. This last constraint greatly complicates the problem of enumerating valid rings. Here, we are interested only in $0 \le m \le 6$ (*i.e.* cones), although other interesting $m$ values also occur, such as saddles ($m<0$), closed shells such as buckyballs and nanotubes ($m=12$), and helicoids $m>6$.

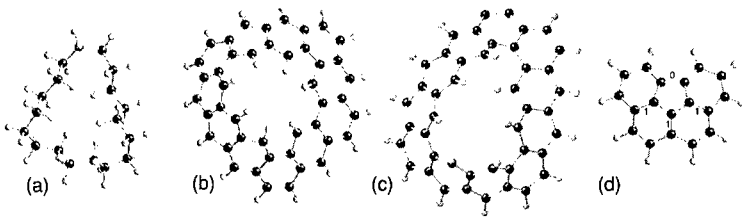


**Figure 3:** a) A flexible $C_{18}H_{36}$ hydrocarbon ring. b) and c) are two growth modes of graphite onto the outside of the ring, each producing an $m$=2 disclination. Pentagons have yet to appear, yet the disclination is essentially fixed. d) Cross-linking in a $C_{18}$ ring. Internal linkages "1" can not create an odd number of pentagons. Outside linkages "0" can.

Figures 3b and 3c show two of the 16,812 possible ways that 6-rings can be added to a $C_{18}$ ring to form a graphitic annulus corresponding to an $m$=2 cone. In each instance, the tip structure is not yet resolved, and pentagons have not yet been formed. However, the enclosed disclination is now fixed because the stiffened annulus has already lost many of its conformational degrees of freedom. The stiffened seed is now committed to a particular value of $m$. Tip closure, with pentagon creation, will occur early in the growth stage, but *after* nucleation of the disclination.

Table 1 lists the number of unique degrees of freedom available to an open $n$-ring ($5 \le n \le 30$) for each of the seven disclinations, $0 \le m \le 6$. We assume that a minimum ring size is required for each disclination. 6, 5, 12, 15, 18, 19 and 18 are the minimum circuit sizes that can circumscribe $m$=0 to 6 unconnected pentagons in a manner consistent with the isolated pentagon rule.

The Table shows that for the smallest open ring sizes, $n$, small $m$-values are favored. In this

| $n$ \ $m$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| 5 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| 6 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 7 | 0 | 3 | 0 | 0 | 0 | 0 | 0 |
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 9 | 0 | 14 | 0 | 0 | 0 | 0 | 0 |
| 10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11 | 0 | 56 | 0 | 0 | 0 | 0 | 0 |
| 12 | 4 | 0 | 217 | 0 | 0 | 0 | 0 |
| 13 | 0 | 203 | 0 | 0 | 0 | 0 | 0 |
| 14 | 7 | 0 | 738 | 0 | 0 | 0 | 0 |
| 15 | 0 | 724 | 0 | 2,141 | 0 | 0 | 0 |
| 16 | 16 | 0 | 2,500 | 0 | 0 | 0 | 0 |
| 17 | 0 | 2,532 | 0 | 7,076 | 0 | 0 | 0 |
| 18 | 108 | 0 | 16,812 | 0 | 34,588 | 0 | 182 |
| 19 | 0 | 17,396 | 0 | 46,496 | 0 | 73,878 | 0 |
| 20 | 280 | 0 | 55,984 | 0 | 112,120 | 0 | 5,606 |
| 21 | 0 | 59,170 | 0 | 152,214 | 0 | 237,950 | 0 |
| 22 | 792 | 0 | 185,548 | 0 | 362,988 | 0 | 48,980 |
| 23 | 0 | 199,524 | 0 | 496,918 | 0 | 766,018 | 0 |
| 24 | 2,272 | 0 | 612,198 | 0 | 1,173,640 | 0 | 257,988 |
| 25 | 0 | 668,266 | 0 | 1,618,324 | 0 | 2,464,636 | 0 |
| 26 | 6,578 | 0 | 2,012,520 | 0 | 3,790,538 | 0 | 1,090,656 |
| 27 | 0 | 2,225,998 | 0 | 5,260,062 | 0 | 7,925,938 | 0 |
| 28 | 19,040 | 0 | 6,595,974 | 0 | 12,230,748 | 0 | 4,142,762 |
| 29 | 0 | 7,381,624 | 0 | 17,068,368 | 0 | 25,476,758 | 0 |
| 30 | 55,750 | 0 | 21,563,852 | 0 | 39,431,494 | 0 | 14,902,092 |

Table 1: The number of modes of an open carbon ring of $n$ atoms that correspond to a disclination of order $0 \le m \le 6$. $n$-rings are not necessarily enclosing pentagons at this stage. Tip restructuring can occur after the disclination is committed during the growth phase.

open ring model, even-numbered rings $n$ can only nucleate even-numbered disclinations $m$. Conversely, odd-numbered rings can only nucleate odd-numbered disclinations. With increasing $n$ ($n \leq 17$), the degrees of freedom are maximum for the $m = 1, 2, 3$ disclination values. For $n \geq 18$, the distribution peaks for $m \geq 3$.

The Table also shows that large, topologically flexible, carbon rings favor the nucleation of cones rather than sheets. Cones with higher enthalpies of formation are favored because the Gibbs free energy is reduced by the increase in entropy associated with the large number of growth modes that encode cones.

More sophisticated ring-counting techniques allow us to count cross-linked modes more efficiently. There is no room here to describe our algorithm or results. The most significant result is that cross-linking of "0" bonds permits even $n$-rings to create odd-$m$ disclinations, and vice-versa (e.g. Fig 3d). The inclusion of cross-linked seeds does not change significantly the relative distribution of modes given in Table 1.

Data on the KVR sample [1] reveal a bimodal distribution of cones, with a broad peak in the $m$=2,3,4 region, and a dominant peak at $m$=0, the planar graphitic disks. Cylinders ($m$=6) occur relatively infrequently. This distribution could be explained by the presence of a relatively dilute concentration of $C_n$ rings in an abundant supply of graphitic carbon building units (*i.e.* C monomers, $C_2$ dimers etc). Self-assembly of the smaller carbon building units will inevitably favor the formation of graphite, which is the lowest energy state for $sp^2$ carbon. This growth mode should produce prolific quantities of graphitic sheets. A secondary growth mode involves the accretion of the smaller carbon building units onto the $C_n$ rings. This latter growth mode clearly favors cones when $n \leq 30$. There is a third possible growth mode where rings collide with rings. This would be equivalent to the ring-stacking model of Wakabayashi and Achiba (1992) [6]. However, if monocyclic rings are dilute, this growth mode will not dominate.

The spheroidal particles commonly found in carbon black are suppressed in the KVR sample. This may be because their seeds are rapidly consumed by cone production. Ebbesen [7] has pointed out that the growth phase is probably much more rapid than the nucleation phase, since seed formation is a slow and difficult process. A high purity and yield of cones can occur if the carbon vapor/plasma is presented with ready-made flexible seeds or nuclei that possess many topological degrees of freedom. Unfortunately, the KVR synthesis conditions are unknown.

Clearly, there may be more than one nucleation mechanism present. 5-rings, as well as 6-rings and the larger $n$-rings, are likely to be present in the plasma/vapor. 5-rings, when present at high concentration, could accrete to form cup-like structures. The KVR sample does show some $m$=2 cones in which pentagons are separated by distances more than a micron, implying that two $m$=1 cones have merged. However, accretion alone can not so clearly explain the observed distribution of angles in cones with relatively sharp tips (*i.e.* pentagons closely spaced).

Figure 3 shows the distribution in $m$-values for Gaussian distributions of seed ring sizes,

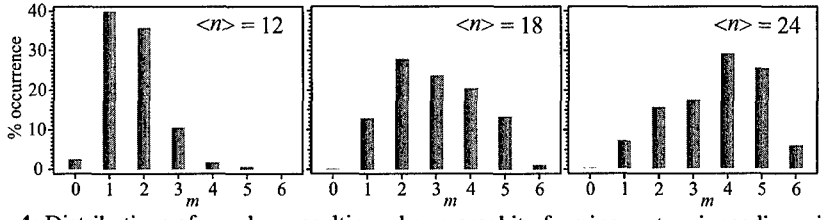


**Figure 4:** Distributions of $m$ values resulting when a graphite-forming system is seeding with Gaussian distributions of monocyclic carbon rings, peaked at $C_{12}$, $C_{18}$ and $C_{24}$ rings respectively. The standard deviation is $\sigma_n = 3$ in each case.

$\langle n \rangle$=12, 18 and 24, with $\sigma_n$ = 3 in each case. Each distribution strongly favors cones, $1 \leq m \leq 5$, with the peak shifting to higher $m$ as $\langle n \rangle$ increases. A histogram for $\langle n \rangle$=20, $\sigma_n$ = 3 (not shown), which peaks at $m$=3, is qualitatively similar to that observed for the KVR sample.

There is negligible production of $m$=0 disks in these histograms. As explained above, disks can be formed in a separate nucleation process, with no large rings necessarily involved.

The validity of the designability argument does not rely on the assumption that monocyclic carbon rings are the seeds. Any flexible seed that is allowed to explore its topological degrees of freedom may suffice. We note that similar "designability" arguments, applied to peptide chains, have been used to explain the thermodynamic stability of certain folded protein structures [3].

The $m$<0 hyperboloidal structures, with negative Gaussian curvature, are not observed in the KVR sample, even though they are abundantly present as potential $C_n$ ring modes. This appears to argue against carbon rings as seeds – they are too flexible. However, it is possible that thermal vibrations will destroy hyperboloidal structures, once seeded. In cones, thermal vibrations will resemble bell modes with the highest stresses near the open cone rim. The cone tip will not be subjected to large stresses. However, in saddle-shaped hyperboloids, the dominant vibration modes will be the "clapping", or "butterfly wing", modes. Such vibrations may subject the high curvature cores of the disclinations to large tensile stresses, ripping such hyperboloids apart. In addition, the more steeply inclined $-6 \leq m \leq -4$ structures may cross-link at their open rims (literally clapped shut), leaving an unrecognizable mass. The $m$>0 cones are expected to be relatively stable to thermal vibrations, which may explain their survival in the KVR sample.

A consequence of our designability model is that pentagon creation becomes a structural tidying-up step that happens *after* the disclination is committed. In the "pentagon road" model [8], pentagons are formed in seed structures in order to eliminate high-energy dangling bonds, and as an annealing mechanism to reduce the overall energy of the structure. In that model, the creation of the pentagon implies the creation of the disclination. The designability argument and the pentagon road model are not in conflict. The designability mechanism implicitly refers to an earlier instant in the seed's existence, when it still possesses topological degrees of freedom. Disclinations are inherently present as conformational modes, but are not yet committed. Pentagons have yet to be formed. In a topologically flexible seed the pentagons appear "along the road", rather than at the beginning. The number of pentagons in the later seed structure is predetermined by the mode committed to by the seed at an earlier stage of growth.

The pentagon road model provides a mechanism for minimizing the enthalpy of seed structures. By incorporating the concept of designability, the pentagon road model can be extended to include entropy, which drives the emergence of preferred graphitic structures.

## ACKNOWLEDGMENTS

We wish to thank Thomas Ebbesen and Ned Wingreen for stimulating discussions.

1. A. Krishnan, E. Dujardin, M.M.J. Treacy, J. Hugdahl, S. Lynum, and T.W. Ebbesen, *Nature* **388**, 451 (1997).
2. M. Ge and K. Sattler, *Chem. Phys. Letts.* **220**, 192 (1994).
3. H. Li, R. Helling, C. Tang, and N. Wingreen, *Science* **273**, 666 (1996).
4. A.T. Balaban, D.J. Klein, and X. Liu, *Carbon* **32**, 357 (1994).
5. S. Ihara, S. Itoh, K. Akagi, R. Tamura, and M. Tsukuda, *Phys. Rev. B* **54**, 14713 (1996).
6. T. Wakabayashi and Y. Achiba, *Chem. Phys. Letts.* **190**, 465 (1992).
7. T.W. Ebbesen, Personal communication (1997).
8. R.E. Smalley, *Acc. Chem. Res.* **25**, 98 (1992).