

Pentaheptite Modifications of the Graphite Sheet

M. Deza,[†] P. W. Fowler,^{*,‡} M. Shtogrin,[§] and K. Vietze[‡]

CNRS and DMI, Ecole Normale Supérieure, 45 rue d'Ulm, 75230 Paris, France, Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, U.K., and Steklov Mathematical Institute, 8 Gubkin Street, 117966 Moscow GSP-1, Russia

Received January 30, 2000

Pentaheptites (three-coordinate tilings of the plane by pentagons and heptagons only) are classified under the chemically motivated restriction that all pentagons occur in isolated pairs and all heptagons have three heptagonal neighbors. They span a continuum between the two lattices exemplified by the boron nets in ThMoB₄ (*cmm*) and YCrB₄ (*pgg*), in analogy with the crossover from cubic-close-packed to hexagonal-close-packed packings in 3D. Symmetries realizable for these pentaheptite layers are three strip groups (periodic in one dimension), *p1a1*, *p112*, and *p111*, and five Fedorov groups (periodic in two dimensions), *cmm*, *pgg*, *pg*, *p2*, and *p1*. All can be constructed by simultaneous rotation of the central bonds of pyrene tilings of the graphite sheet. The unique lattice of *cmm* symmetry corresponds to the previously proposed pentaheptite carbon metal. Analogous pentagon-heptagon tilings on other surfaces including the torus, Klein bottle, and cylinder, face-regular tilings of pentagons and *b*-gons, and a full characterization of tilings involving isolated pairs and/or triples of pentagons are presented. The Kelvin paradigm of a continuum of structures arising from propagation of two original motifs has many potential applications in 2D and 3D.

1. INTRODUCTION

Novel forms of carbon have excited much experimental and theoretical interest over the past two decades.^{1–12} Matched heptagonal and pentagonal rings have been considered as means of accounting for negative local curvature, bends,^{13,14} and tapers in nanotube tips,¹⁵ creating tori of low strain,¹⁶ and rounding out the facets of polyhedral onion-like particles.¹⁷ In contrast to these dilute distributions of heptagons is one recent proposal for a pentaheptite modification of the graphite sheet in which *all* hexagonal rings are replaced by either pentagons or heptagons, a structure in which carbon would be expected to be metallic.¹⁸

It is clear from the paper by Crespi et al.¹⁸ that many variations on the one highly symmetric structure studied there are possible, and in fact two versions of the pentagon + heptagon tiling of the plane are already chemically realized in another part of the periodic table, in the boron nets of the ternary borides ThMoB₄ and YCrB₄¹⁹ (Figure 1), opening up the distant but intriguing prospect of templated synthesis of the as yet unknown carbon materials. Both of these chemical examples are *face-regular* (i.e., every pentagon in the tiling has the same number, t_5 , of pentagonal neighbors, and every heptagon the same number, t_7 , of heptagonal neighbors), a property of current interest in the mathematical theory of polyhedra.²⁰

In the present paper we generalize the pentaheptite example, retaining some chemically motivated restrictions, and find a complete classification of these layer materials (section 2). The two nets of Figure 1 are shown to define extremes of a continuum, in a two-dimensional analogy to the relationship among cubic-close-packed (ccp), hexagonal-

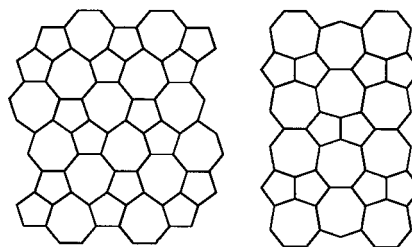


Figure 1. Two chemical pentaheptite nets.¹⁹ Boron nets in YCrB₄ (left) and ThMoB₄ (right). Every ring is either pentagonal or heptagonal, and the tiling is face-regular with $t_5 = 1$ and $t_7 = 3$ (see the text).

close-packed (hcp), and intermediate packings of spheres in three dimensions (see, for example, ref 19). Allowed symmetry groups are listed (section 3), and construction via the generalized Stone–Wales transformation is given (section 4). In the remaining sections, extensions in three directions are described: for face-regular structures involving pentagons and *b*-gons (section 5), pentaheptites on other surfaces including analogues of the nanotubes (section 6), and a general characterization theorem for tilings that involve isolated pairs and/or isolated triples of pentagons (Appendix).

2. CHARACTERIZATION OF STRUCTURES

A pentaheptite is taken to be a tiling of the Euclidean plane by pentagons and heptagons that is cubic, i.e., such that three edges meet at each vertex. With reference to the geometrically flat graphite sheet, the two types of nonhexagonal face introduce curvature: positive for pentagons and negative for heptagons. It has been argued¹⁸ that the physically interesting case will be where the pentagons occur as isolated pairs. It turns out (see the Appendix for the proof of a more general classification theorem) that *any* face-regular penta-

[†] Ecole Normale Supérieure.

[‡] University of Exeter.

[§] Steklov Mathematical Institute.

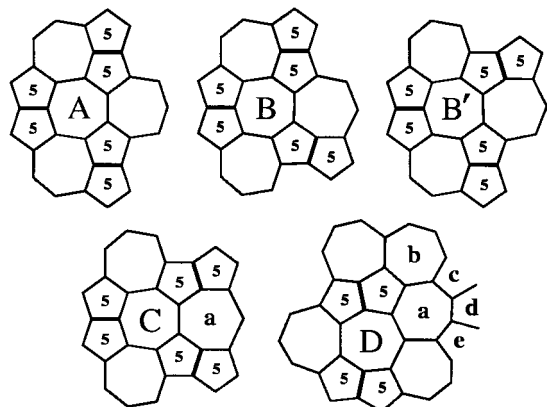


Figure 2. Conceivable local environments A–D of heptagons in a pentaheptite sheet with $t_5 = 1$ and $t_7 = 3$. Note that a single D motif implies violation of the isolated-pentagon-pair rule: heptagon a already has at least two heptagonal neighbors in the D patch, and if face b were a pentagon, it would produce a linear pentagon triple, but if face b is a heptagon, then $t_7 = 3$ implies that all remaining neighbors c, d, and e are pentagons, and hence the linear triple is unavoidable.

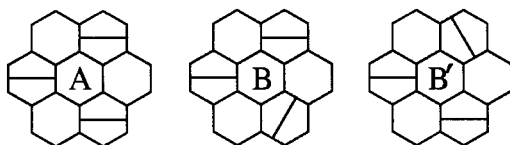


Figure 3. Reduction of motifs to decorations of combinatorial graphite hexagon patches. The bars in the hexagons represent pentagon–pentagon fusions; central heptagons A and B are now hexagons with a bar incident on one edge. Notice that this incident bar is parallel to one other in B and B', whereas all three are parallel in A.

heptite in which all pentagons occur in isolated pairs has $t_5 = 1$ and $t_7 = 3$. Thus the objects to be studied are (1,3)-pentaheptites.

Consideration of the immediate environment of a heptagon shows that there are five possible first-neighbor shells (“coronas”) of pentagon pairs and heptagons, two of which (B, B') form a mirror-image pair. These five motifs are listed in Figure 2. Not all may exist in a (1,3)-pentaheptite tiling: Case C implies case D for a neighbor of the central heptagon, but case D is forbidden because it in turn implies violation of the isolation of pentagon pairs. Thus, the patterns for the whole layer can contain *only* local motifs A and/or members of the B chiral pair. This turns out to be a key simplification because both A and B can be represented on the graphite lattice itself, simply by reducing each pentagon pair to a barred hexagon so that each motif becomes a decorated coronene fragment (Figure 3), and the empty hexagons represent the heptagons of the pentaheptite.

Now consider how the individual motifs A and B may pack to cover the plane. It is clear that choosing a given heptagon as the center of a B motif immediately forces two of its three heptagonal neighbors to adopt a B configuration of the same handedness. Therefore, a linear chain of B centers propagates to infinity in both directions. Motifs of type A also have this propagation property (Figure 4).

Instead of considering strips of A or B heptagons, it is useful to concentrate on the pentagon pairs in the decorated sheet, which form infinite chains of 1,4 linked barred hexagons. Such chains are either α (all bars running from top left to bottom right) or β (all bars running up to top right).

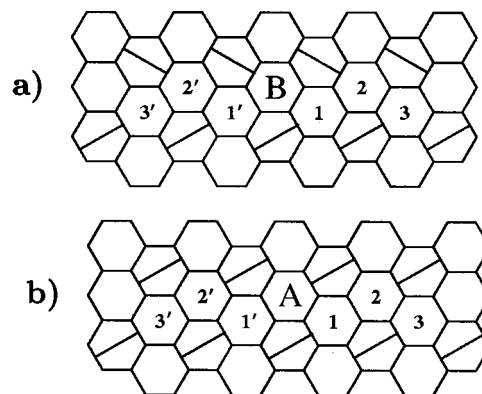


Figure 4. (a) Propagation of B motifs in infinite linear strips. Fixing the hexagon labeled B fixes bars in its three (pentagon-pair) neighboring hexagons; 1 now has an incident bar, but not a parallel pair, fixing the missing bar in orientation, and is of the B type. Likewise the missing bar for face 2 cannot be incident, and 2 is also of the B type. Iteration of this argument sends the chain of B heptagons off to infinity in both directions. By reflection, B' has the same property. (b) A motifs have parallel bars and hence also propagate to infinity.

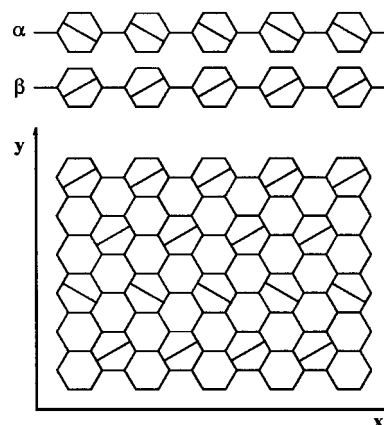


Figure 5. Description of the pentaheptite plane in terms of barred-hexagon (pentagon-pair) chains α and β . The plane has translational symmetry along, x but the behavior along y depends on the sequence of α and β chains. The example shown is $\dots\beta\beta\alpha\beta\dots$.

B or B' strips are bordered by one α chain and one β chain, whereas A strips are bordered either by two α chains or two β chains.

All (1,3)-pentaheptites can thus be represented in two ways, as the two-dimensional graphite plane striped by A's and B's, and also as one-dimensional infinite words in the two-letter alphabet of α and β (Figure 5). Clearly, there is a one-to-one correspondence between these infinite words and the (1,3)-pentaheptite tilings, and the stacking picture also demonstrates that the allowed tilings span a continuum from fully uniform $(\alpha)_\infty \equiv \dots\alpha\alpha\alpha\dots \equiv (\beta)_\infty$ to fully alternating $(\alpha\beta)_\infty \equiv \dots\alpha\beta\alpha\beta\dots$, in a manner reminiscent of the description of ccp, hcp, and the infinite number of intermediate tilings of 3D space by layers of regular tetrahedra and regular octahedra.

3. SYMMETRY GROUPS

Given that all (1,3)-pentaheptites are periodic in one dimension, two cases are possible: either the plane is an aperiodic stack of strips which has a *strip group*, or the stacking itself is periodic and has a *Fedorov plane group* (see, for example, ref 19 or 21).

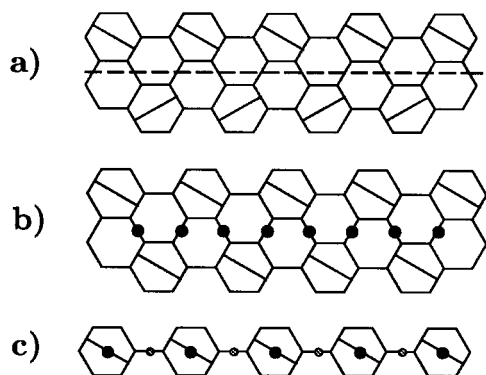


Figure 6. Examples of strip groups for (1,3)-pentaheptites: (a) $p1a1$, e.g., ... $\alpha\beta\beta\alpha\beta\beta\alpha\beta.\alpha\beta\alpha\alpha\beta\alpha\alpha\beta...$; (b) $p112$, centered between strips, e.g., ... $\beta\alpha\alpha\alpha\beta\alpha\alpha\beta.\alpha\beta\alpha\alpha\beta\alpha\alpha\beta...$; (c) $p112$, centered in a strip, e.g., ... $\beta\beta\alpha\beta\alpha(\alpha)\alpha\beta\alpha\beta\beta...$

Just three strip groups are possible in our case (Figure 6). These are (i) the glide-reflection symmetry group $p1a1$, when the aperiodic word is symmetric about its center under $\alpha \leftrightarrow \beta$ exchange, (ii) the binary rotational symmetry group $p112$, when the word is symmetric about its center under $\alpha \leftrightarrow \alpha$ and $\beta \leftrightarrow \beta$ exchange (realized in one of two ways as the center is either within a strip or between two strips), (iii) the trivial symmetry $p111$. All other strip groups are ruled out by the fact that a word containing both α and β cannot exhibit reflection symmetry.

When the stack of strips is periodic, the allowed Fedorov groups are again limited. Eight of the seventeen groups are eliminated immediately because they contain a rotational axis of order greater than two, and four more are eliminated by the lack of reflection symmetry of α, β mixed stacks. The remaining five groups are all realizable. They are (i) $cm\bar{m}$, as in ThMoB_4 , which is uniquely realized by $(\alpha)_\infty = (\beta)_\infty$, and is the only (1,3)-pentaheptite group to contain a reflection, (ii) pgg , the symmetry of the YCrB_4 layer, (iii) pg , (iv) $p2$, and (v) $p1$, the pure translational group. In $cm\bar{m}$, all pentagons are equivalent, as are all heptagons.

Figure 7 illustrates the minimal and next-to-minimal examples for each plane group, and shows the Bravais cell for each case. Note that, although $p1$ and $p2$ admit in principle arbitrary angles in the Bravais cell, here they give an orthogonal cell or a nonorthogonal cell with specific angles depending on the parity and length of the repeat unit of the (α, β) word.

4. RELATION WITH THE STONE–WALES TRANSFORMATION

Crespi et al.¹⁸ note that their pentaheptite candidate for metallic carbon can be obtained by simultaneous application of bond rotation to four-hexagon pyrene units over the whole graphite plane, and comment that this will be true of many others. Given that the α, β strips are obtained by making one of two distinct partitions of a quadruple strip of hexagons into pyrene units and then rotating all central bonds (Figure 8), we can go further. All (1,3)-pentaheptites can be constructed by this simultaneous generalized Stone–Wales¹¹ transformation. This implies that all (1,3)-pentaheptites are fully azulenoid in the terminology of Kirby,¹⁰ as they can be tiled by fused pentagon–heptagon pairs. However, this Stone–Wales construction of a given pentaheptite is not

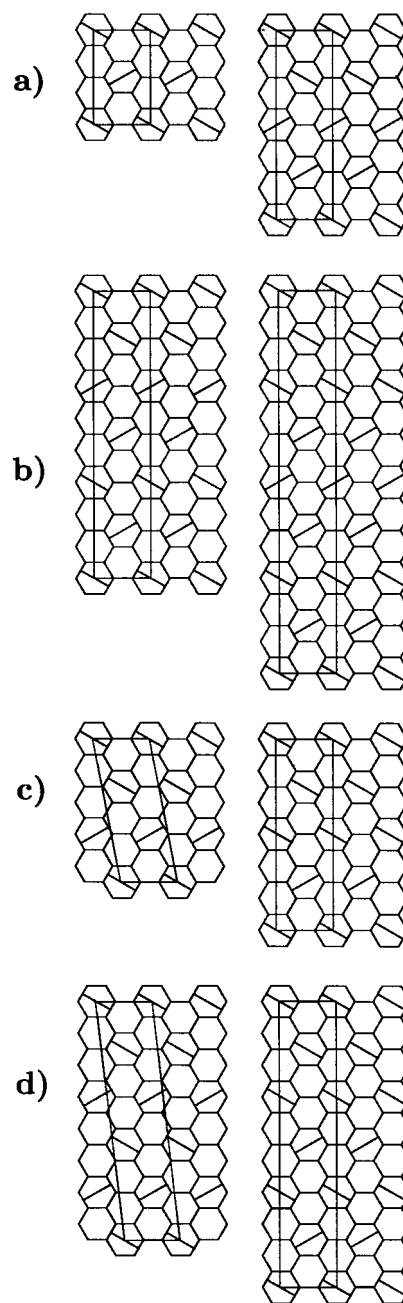


Figure 7. Examples of plane groups for (1,3)-pentaheptites. $cm\bar{m}$ (the right-hand pattern in Figure 1) is unique, but for each of the other groups the minimal and next larger examples are shown: (a) pgg , e.g., $(\alpha\beta)_\infty$ and $(\alpha\alpha\beta\beta)_\infty$; (b) pg , e.g., $(\alpha\alpha\beta\beta\alpha\beta)_\infty$ and $(\alpha\alpha\alpha\beta\beta\beta\alpha\beta)_\infty$; (c) $p2$, e.g., $(\alpha\alpha\beta)_\infty$ and $(\alpha\alpha\alpha\beta)_\infty$; (d) $p1$, e.g., $(\alpha\alpha\beta\alpha\beta)_\infty$ and $(\alpha\alpha\alpha\beta\alpha\beta)_\infty$.

unique, as different partitions into pyrene tiles may yield the same product on bond rotation.

Furthermore, bond rotation can produce structures outside the (1,3)-pentaheptite, both periodic and nonperiodic, some including hexagonal faces. An infinite series of pentagon–hexagon–heptagon tilings with separated nonhexagonal faces can also be produced by Goldberg scaling of any given (1,3)-pentaheptite, as can be done with fullerenes.^{24,25} Structures with a proportion of hexagons as well as pentagons and heptagons do occur experimentally among the ternary borides, and in fact, the Y_2ReB_6 structure in Figure 5.45 of ref 19 can be obtained by periodic Stone–Wales transformations on a graphite sheet tiled with naphthalene and pyrene

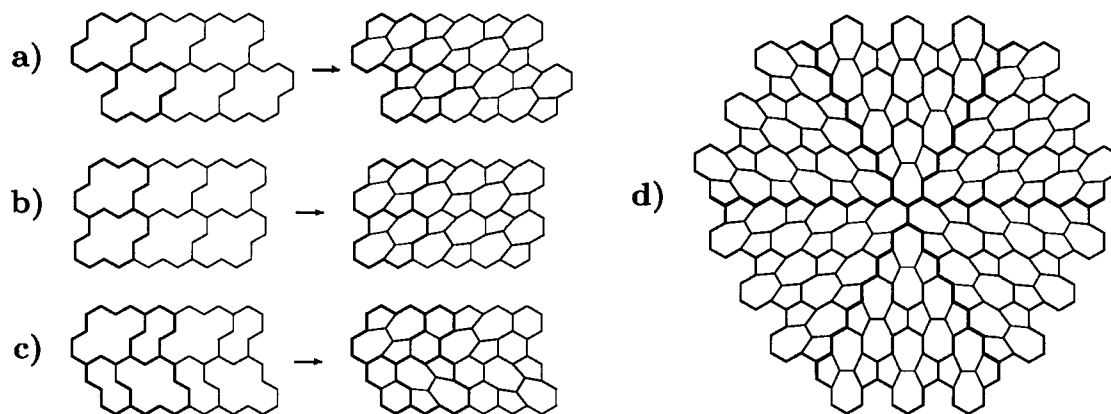


Figure 8. Stone–Wales transformation of pyrene units gives head-to-tail fused couples of pentagon-heptagon pairs (azulene units). Concerted Stone–Wales transformations lead to (a) α or (b) β strips, depending on the choice of pyrene units. (c) A partition of the graphite plane into pyrene and naphthalene tiles leads to the known structure of Y_2ReB_6 ¹⁹ under Stone–Wales transformation of all pyrene units. (d) An aperiodic structure derived from a pure pyrene tiling.

patches (Figure 8c). The resulting structure has *pgg* symmetry, and is face-regular, as each *i*-gon has the same number t_{ij} of *j*-gonal neighbors ($t_{5j} = 0, 2, 3, t_{6j} = 2, 1, 3,$ and $t_{7j} = 3, 3, 1$ for $i = 5, 6, 7$).

An example of an aperiodic pentaheptite constructed by Stone–Wales transformation of a purely pyrene tiling is shown in Figure 8d. This conical defect is centered on a fused triple of exceptional heptagons where each has only two pentagonal neighbors; all other heptagons have four pentagonal neighbors, and all pentagons are still in isolated pairs. This structure fits case ii of the classification theorem given in the Appendix.

It is also interesting to note that the Stone–Wales transformation of certain fullerenes can produce spherical analogues of the pentaheptites. Transformation of all 30 pyrene patches of the icosahedral C_{60} fullerene gives one of the two icosahedral *fulleroids* constructed by Dress and Brinkmann.²⁶

5. OTHER FACE-REGULAR TILINGS OF THE PLANE WITH PENTAGONS

The two limiting tilings $(\alpha)_\infty$ and $(\alpha\beta)_\infty$ are also interesting mathematically because, of all the (1,3)-pentaheptites, they are the only 2-*isohedral* tilings; i.e., they each have exactly two orbits of faces, one of pentagons and one of heptagons. For tilings where all faces have one of two sizes, 2-*isohedrality* implies face regularity.

Under the restriction that all vertexes are of the same degree, there are exactly 39 2-*isohedral* tilings of the Euclidean plane (see the list in ref 27). Only seven of those with degree 3 involve pentagons (Figure 9). The first two are our $(\alpha)_\infty$ and $(\alpha\beta)_\infty$. The next two are also pentagon–heptagon tilings, but with (t_5, t_7) signature (2,4), the first with all pentagons in isolated fused triples, the second with all pentagons in infinite strips separated by double strips of heptagons.

In fact, $(t_5, t_7) = (1,3)$ and (2,4) are the only possible signatures of face-regular pentaheptites. We must have $t_7 = t_5 + 2$, because the ratio of 5- and 7-gons is $1 = (7 - t_7)/(5 - t_5)$, but cases $t_5 = 0, 3, 4,$ and 5 are impossible. For example, if $t_5 = 3$, any 5-gon has exactly two (mutually adjacent or not) 7-gonal neighbors, but each of them has more than two 5-gonal neighbors.

In the case of signature (2,4), the pentagons are organized either as isolated fused triples or in infinite strips, since no *finite* cycle of 5-gons can be filled by 7-gons, so that any vertex has degree 3 and any 7-gon is adjacent to exactly two 5-gons. Clearly, the infinite strips of pentagons should be parallel, and the only possibility is tiling d of Figure 9.

Finally, one can check that any cubic face-regular tiling of the Euclidean plane by 5- and *b*-gons only (where $b > 7$) (i.e., a *penta-b*-tite) has either $(b; t_5, t_b) = (12 - i; 3, i)$, where $0 \leq i \leq 4$, or it has $(b; t_5, t_b) = (8; 2, 2)$. Examples (all 2-*isohedral*) are known for the cases (8; 2, 2) and (12; 3, 0); these are tilings e–g of Figure 9.

The theory developed here for pentaheptites with isolated pairs of pentagons will be applicable in a similar form to the case where all pentagons occur in isolated fused *triples*. It turns out (see the Appendix) that isolated-triple pentaheptites are all face-regular, with signature $(t_5, t_7) = (2,4)$. One can check that the corona of any heptagon is then one of two types, E and the mirror pair F, F' (Figure 10). Moreover, each corona propagates (it is enough to check this for F), so that a continuum of lattices made up of two types of strips, ϵ and ϕ , can be constructed in exact analogy with the (1,3)-pentaheptites, the ternary borides, and the 3D packings of spheres. The two extreme cases which play the roles of $(\alpha)_\infty$ and $(\alpha\beta)_\infty$ are now $(\epsilon)_\infty \equiv (\phi)_\infty$ and $(\epsilon\phi)_\infty$. $(\epsilon)_\infty$ is unique in having symmetry *cm* and is the unique 2-*isohedral* isolated-triple pentaheptite; $(\epsilon\phi)_\infty$ is not 2-*isohedral*, as both pentagons and heptagons fall into two distinct orbits. The enumeration of allowed symmetry groups proceeds as before.

In carbon structures, grouping of pentagons in isolated triples is less attractive energetically than simple pairing. The considerably greater strain energy of the lattice with embedded triples is likely to induce rumpling or buckling of the topologically planar sheet. Heteroatomic decoration of isolated-triple pentaheptites is perhaps a more likely option for their chemical realization.

The isolated-pentagon and isolated-triple pentaheptites can be put in a much more general context, as examples of the Kelvin paradigm:²⁸ a continuum of structures is described by words in a two-letter alphabet (α, β) based on propagating motifs, where each intermediate structure satisfies a local regularity criterion, and the two end-point structures may satisfy some stronger global criterion. In our pentaheptite

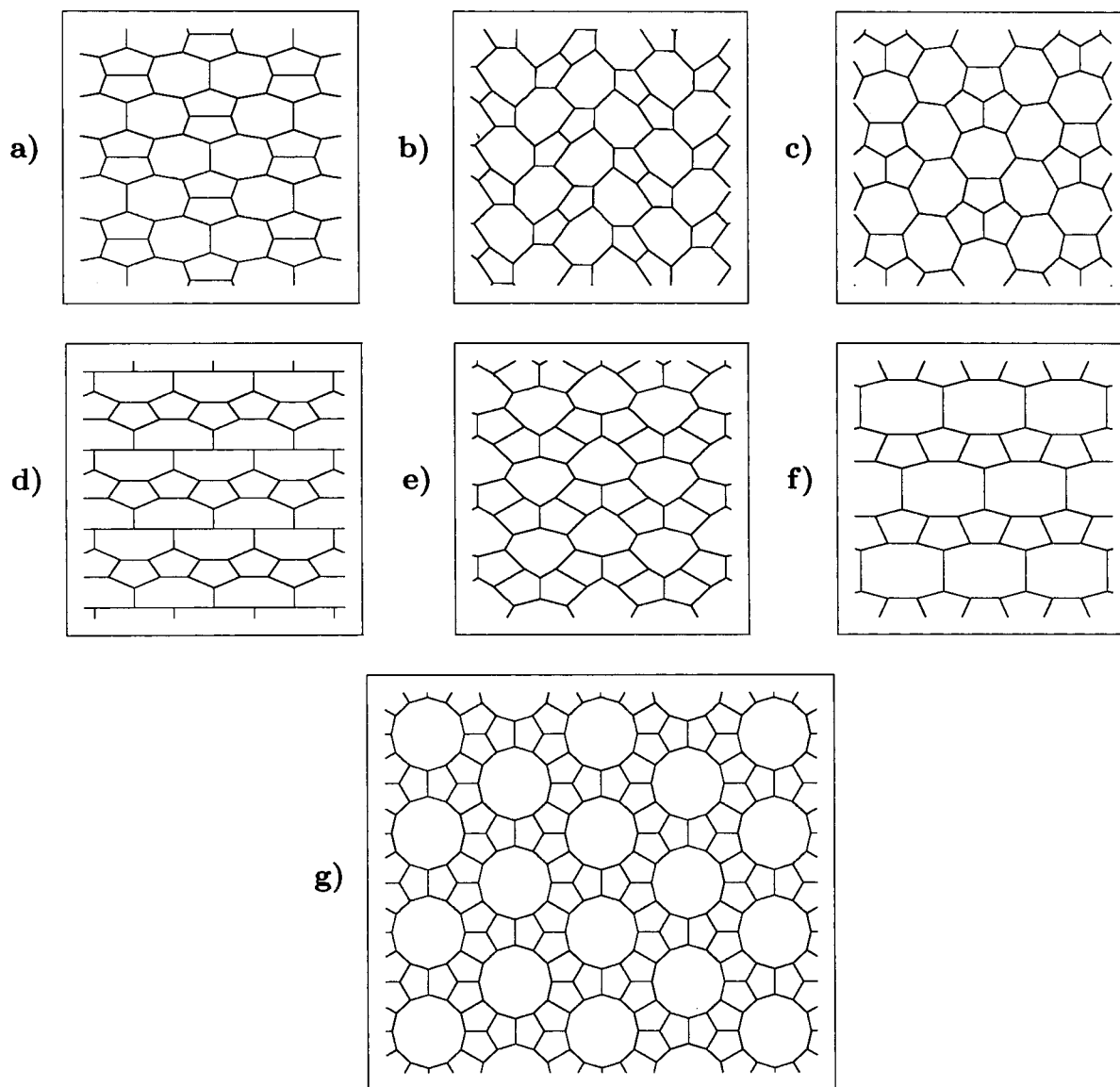


Figure 9. The seven cubic, 2-isohedral tilings of the Euclidean plane by pentagons and *b*-gons.

cases, the local criterion is face regularity with a fixed (t_5, t_7) signature, and the global criterion is minimality of the number of orbits of faces. In fact, a third instance of this general pattern can be deduced from Figure 9. Tilings 9e and 9f are of (2,2)-pentaoctites, i.e., cubic tilings of the Euclidean plane with 5- and 8-gons which are face-regular with signature $(t_5, t_8) = (2, 2)$. These two cases are the limits of a continuum where every structure is generated by parallel repetition of interleaved pentagonal and octagonal “snakes” (infinite paths). One can check that every (2,2)-pentaoctite can be generated in this way. Each structure is defined by choice of an infinite sequence of left/right turns in the snakes (i.e., a word in the α, β alphabet). In ref 28, four cases of the continuum paradigm in three dimensions are described (partitions 31–34 of Table 4). Partitions 33 and 34 show a transition from local to global regularity. Further aspects of this general picture will be addressed elsewhere.

6. PENTAHEPTITES ON OTHER SURFACES

All the structures considered so far are decorations of the Euclidean plane and are in a sense small departures from the graphite paradigm. However, there is great chemical and

physical interest in carbon tilings of other surfaces, in particular the sphere (as in the fullerenes³) and the open-ended cylinder (as in nanotubes²⁹). Extension to surfaces of higher genus^{9,10,30} and even to nonorientable surfaces³¹ has been explored in the literature for pentagon–hexagon networks. A similar and even simpler classification can be made starting from the pentaheptites.

The following surfaces arise as *quotients* of the Euclidean plane:³³ the torus (T^2), Klein bottle (K^2), infinite cylinder (C^2), and Möbius surface (M^2 , also called the twisted cylinder). Given a tiling of the plane, we can collapse it onto one of the listed surfaces if an appropriate normal subgroup of the symmetry group of the tiling can be found. Such a subgroup is generated by two translations (T^2), one rotation and one glide-reflection (K^2), one translation (C^2), or one glide-reflection (M^2).

Desirable tilings are *cell-complex* (polyhedral) maps, i.e., those where the intersection of any two faces is an edge, a vertex, or empty and the intersection of two edges is a vertex or empty. To give a polyhedral map, a generator should therefore not have too small a translational period.

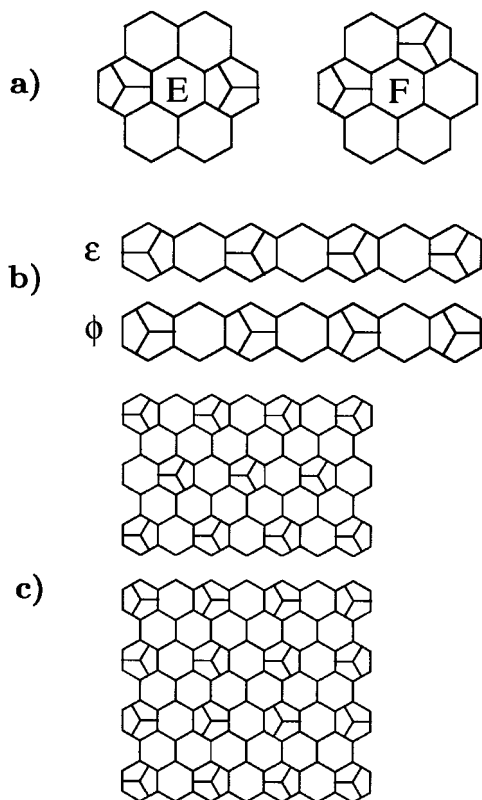


Figure 10. Classification of isolated-triple (IT) pentaheptites: (a) the two possible coronas E and F of a heptagon in an IT-pentaheptite; (b) propagation leads to two possible infinite strips, ϵ and ϕ ; (c) extremal IT-pentaheptites $(\epsilon)_{\infty}$ and $(\epsilon\phi)_{\infty}$.

Recall that for our (1,3)-pentaheptites there are only three strip and five plane symmetry groups. No strip group can yield T^2 or K^2 . The groups $p111$, $p112$, and $p2$, $p1$ cannot give K^2 or M^2 , as all four lack glide-reflections. Tilings on T^2 and K^2 are finite, with equal numbers of pentagons and heptagons ($p_5 = p_7$) and a vertex count of $v = 4p_5 = 4p_7$. From the allowed starting symmetry groups, it can be shown that the smallest cell complexes on T^2 have $p_5 = 6, 8, 24, 12,$ and 20 for $cm\bar{m}$, pgg , pg , $p2$, and $p1$, respectively. Similarly, on K^2 the smallest examples have $p_5 = 4, 6,$ and 18 for groups $cm\bar{m}$, pgg , and pg (Figure 11). It turns out that the four-pentagon structure derived from the $cm\bar{m}$ group is the smallest polyhedral K^2 -pentaheptite without restriction on the (t_5, t_7) signature. An even smaller but nonpolyhedral K^2 -pentaheptite with three pentagons can be derived from $(\epsilon)_{\infty}$; its dual map has graph K_6 , i.e., the six-color map on the Klein bottle.

Pentaheptite tilings on C^2 are direct analogues of the well-known graphitic nanotubes. Versions of the $cm\bar{m}$ (1,3)-pentaheptite rolled onto the cylinder were mentioned in ref 18, where it was stated that all such tubes would be metallic. Any (1,3)-pentaheptite can be rolled up in this way. For example, all three strip groups give minimal polyhedral tubes on C^2 with two pentagonal pairs on the circumference (two solutions for $p112$, unique solutions for the other two groups). Cylinders with two, three, four, ... pentagon pairs on the circumference are possible; in the case of $p1a1$ polyhedral Möbius tubes are generated by odd powers i (≥ 3) of the generating glide-reflection.

Finally, we note that face regularity itself is a strong condition for finite polyhedra, i.e., for tilings of the sphere,

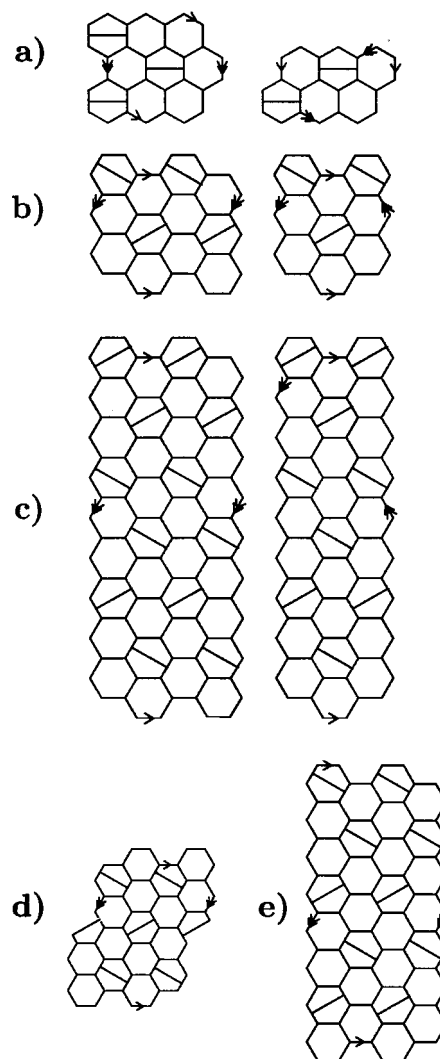


Figure 11. (1,3)-Pentaheptite analogues on the torus and Klein-bottle surfaces, in each case the smallest that can be derived from the plane symmetry group (see the list in the text). Arrows on the periphery of each patch indicate the rules for gluing to give the T^2 (K^2) surface. T^2 (left) and K^2 (right) pentaheptites from (a) $cm\bar{m}$, (b) pgg , and (c) pg and T^2 -pentaheptites from (d) $p2$ and (e) $p1$.

S^2 . There are exactly three face-regular pentagon + heptagon cubic polyhedra (Figure 12). They have 28, 44, and 92 vertexes, their (t_5, t_7) signatures are (4,0), (3,1), and (2,2), and their point groups are D_{7d} , D_{3h} , and C_{3v} , respectively.

Extension to the general case of cubic, face-regular pentagon + b -gonal polyhedra adds only one infinite family and a finite number of new polyhedra.²⁰ The infinite family is of barrels, one for each $b \geq 3$, where two b -gons are separated by two layers of pentagons. The finite set of extra polyhedra are for $b = 6$ a further eleven fullerenes, for $b = 7$ the three described above, for $b = 8$, two more polyhedra, and for $b = 10$ a single icosahedrally symmetric polyhedron. Thus, the set of face-regular cubic polyhedra includes the first four icosahedral members of the fullerene series, C_{20} , C_{60} , C_{80} , and C_{140} ; all other icosahedral fullerenes have at least two hexagon environments, though their pentagons always form a single orbit.³

7. CONCLUSION

Restriction of the pentaheptite definition to (1,3) face-regular lattices has been shown to lead to a full classification

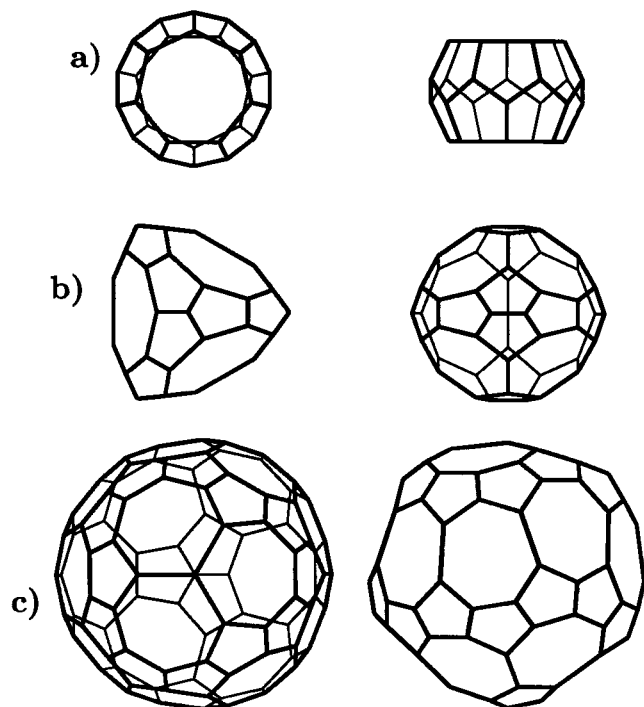


Figure 12. The three spherical face-regular pentaheptite polyhedra (a) C_{28} , (b) C_{44} , and (c) C_{92} , all shown in two orthogonal projections.

of these structures. Minimal examples have been provided for all allowed 1D and 2D symmetry groups, each of which could be investigated as a hypothetical alternative to graphite. Generalizations to other surfaces and ring sizes have been introduced, including pentaheptite analogues of the cylindrical nanotubes. The analogous classification of (2,4) pentagon-triple pentaheptites has been sketched.

ACKNOWLEDGMENT

This research was supported by the EU under TMR Network Contract Biofullerenes CT970192, and by the University of Exeter Research Fund. M.S. acknowledges support under Grant 99-01-00010 of the Russian Fund for Fundamental Research.

APPENDIX: A CLASSIFICATION THEOREM

Let T be any cubic tiling of the Euclidean plane by 5-gons and b -gons only. The Euler relation for tilings is applicable here, as T is *normal* and all vertexes are of the same degree.²¹ Call an edge an (s,t) -edge if it is the intersection of an s -gon and a t -gon. Call T an *IP-tiling* if all pentagons are organized in isolated pairs and an *IT-tiling* if all pentagons belong to isolated triples (i.e., fused triples where the three pentagons are pairwise adjacent). Call T an *ITP-tiling* if all pentagons are organized in either isolated pairs or isolated triples. Call a $(b,5)$ -edge *isolated* if it is not incident with another $(b,5)$ -edge of the same b -gon. Note that *nonisolated* $(b,5)$ -edges, if present, occur as pairs in any ITP tiling. Note also that it is possible for two adjacent edges of a pentagon to be isolated $(b,5)$ -edges in this sense. In any ITP-tiling, on deletion of all $(5,5)$ -edges, each pair (triple) of pentagons becomes a hexagon.

Theorem: Let T be a cubic ITP-tiling of the Euclidean plane by 5- and b -gons only. Then T belongs to exactly one of the following three cases.

(i) $b = 7$, T is a decoration of the hexagonal sheet by the set of $(5,5)$ -edges, and any 7-gon has exactly one pair of nonisolated $(7,5)$ -edges. Moreover, (i1) if T is an IP-tiling, then each 7-gon has exactly two isolated $(7,5)$ -edges, and (i2) if T is an IT-tiling, then each 7-gon has exactly one isolated $(7,5)$ -edge.

(ii) $b = 7$, the ratio of the number of 7-gons having zero and two pairs of nonisolated $(7,5)$ -edges is 1:1, such 7-gons exist, and any two 7-gons with two pairs of nonisolated $(7,5)$ -edges are not adjacent.

(iii) $b = 6$, and the number of pentagons p_5 is 0, 2 (an isolated pair), 3 (an isolated triple), 4 (two pairs of pentagons), 5 (a pentagon triple and a pair), or 6 (three pentagon pairs or two triples). For $p_5 \leq 3$, each p_5 gives a unique T ; for $p_5 \geq 4$, each p_5 gives an infinity of tilings T .

Proof: First, $b \geq 6$, since otherwise T is a partition of the sphere. The case $b = 6$ is an instance of plane fullerenes,^{31,32} for which it is known that $p_5 \leq 6$. This is case iii of the Theorem.

From now on, suppose $b \geq 7$. Some b -gon has at least $b - 6$ pairs of nonisolated $(b,5)$ -edges, since otherwise by deleting the $(5,5)$ -edges, we would obtain a tiling by greater-than-6-gons, i.e., a partition of the hyperbolic plane. Only two cases are possible:

(A) Any b -gon has exactly $b - 6$ pairs of nonisolated $(b,5)$ -edges.

(B) Some b -gon has at least $b - 5$ pairs of nonisolated $(b,5)$ -edges.

We will show now that cases A and B are exactly cases i and ii of the theorem.

Consider first case B. A b -gon with at least $b - 5$ pairs of nonisolated $(b,5)$ -edges should also have at least $b - 5$ (b,b) -edges to separate the above pairs. So $b \geq 3(b - 5)$, implying $b = 7$. By deleting the $(5,5)$ -edges from T , we get a partition T' of the Euclidean plane by 5-, 6-, and 7-gons; all 5- and 7-gons of T' come from 7-gons of T having, respectively, two or zero pairs of nonisolated $(7,5)$ -edges. By Euler's formula, the ratio of the number of 5- and 7-gons in T' is 1:1. So we are exactly in case ii of the theorem. It is easy to verify that any two 7-gons with two pairs of nonisolated $(7,5)$ -edges are not adjacent, and therefore that the pentagons in T' will be isolated.

It remains to show that case A is exactly the case i of the Theorem. First, by deleting the $(5,5)$ -edges, we get the hexagonal sheet; i.e., T is a decoration of the graphite plane by the set of $(5,5)$ -edges. By the same argument as in case B, we have $b \geq 3(b - 6)$ in case A. So $b = 7, 8, \text{ or } 9$.

If $b = 9$, then any 9-gon has $b - 6 = 3$ pairs of nonisolated $(9,5)$ -edges, so it has no isolated $(9,5)$ -edges. But any one of the three 9-gons adjacent to such a 9-gon has at least one isolated $(9,5)$ -edge, a contradiction. If $b = 8$, any 8-gon has $b - 6 = 2$ pairs of nonisolated $(8,5)$ -edges; so it has at most one isolated $(8,5)$ -edge. Then T contains some 8-gons with at least one isolated $(8,5)$ -edge, because each 8-gon without isolated $(8,5)$ -edges is adjacent to four that have one such edge. But, any 8-gon with exactly one isolated $(8,5)$ -edge, and hence two pairs of nonisolated $(8,5)$ -edges, is adjacent to an 8-gon with more than one isolated $(8,5)$ -edge, a contradiction. So $b = 7$.

It remains to consider subcases i1 and i2. The number of isolated $(7,5)$ -edges per 5-gon is two for IP- and one for IT-pentaheptites; the ratio of the numbers of 5- and 7-gons

is 1:1 for any pentaheptite on the Euclidean plane. Recall that any 7-gon has exactly one pair of nonisolated (7,5)-edges, i.e., zero, one, or two isolated (7,5)-edges. The number of isolated (7,5)-edges per 7-gon should therefore be on average two for IP- and one for IT-pentaheptite. This can be achieved, in the IP case, only if every 7-gon has two isolated (7,5)-edges. In the IT case, no 7-gon has exactly two isolated (7,5)-edges, since otherwise the 7-gon that separates the two isolated edges has two pairs of nonisolated (7,5)-edges, a contradiction. So, an IT-pentaheptite has on average one isolated (7,5)-edge per 7-gon, while no 7-gon has more than one such edge. Each 7-gon has therefore exactly one such edge. Q.E.D.

REFERENCES AND NOTES

- (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. C₆₀ - Buckminsterfullerene. *Nature* **1985**, *318*, 162–163.
- (2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. Solid C₆₀ - A new form of carbon. *Nature* **1990**, *347*, 354–358.
- (3) Fowler, P. W.; Manolopoulos, D. E. *An Atlas of Fullerenes*; Oxford University Press: Oxford, 1995.
- (4) Iijima, S. Helical microtubules of graphitic carbon. *Nature* **1991**, *354*, 56–58.
- (5) Ugarte, D. Curling and closure of graphitic networks under electron-beam irradiation. *Nature* **1992**, *359*, 707–709.
- (6) Liu, J.; Dai, H. J.; Hafner, J. H.; Colbert, D. T.; Smalley, R. E.; Tans, S. J.; Dekker, C. Fullerene 'crop circles'. *Nature* **1997**, *385*, 780–781.
- (7) Ebbesen, T. W. Cones and tubes: Geometry in the chemistry of carbon. *Acc. Chem. Res.* **1998**, *31*, 558–566.
- (8) Terrones, H.; Mackay, A. L. The geometry of hypothetical curved graphite structures. *Carbon* **1992**, *30*, 1251–1260.
- (9) King, R. B. Chemical applications of topology and group theory 29: Low-density polymeric carbon allotropes based on negative curvature structures. *J. Phys. Chem.* **1996**, *100*, 15096–15104.
- (10) Kirby, E. C.; Mallion, R. B.; Pollak, P. Toroidal polyhexes. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1945–1953.
- (11) Yao, Z.; Postma, H. W. C.; Balents, L.; Dekker, C. Carbon nanotube intramolecular junctions. *Nature* **1999**, *402*, 273–276.
- (12) Li, J.; Papadopoulos, C.; Xu, J. Growing Y-junction carbon nanotubes. *Nature* **1999**, *402*, 253–254.
- (13) Dunlap, B. I. Designing fullerene materials with heptagonal and pentagonal defects. In *The Chemical Physics of Fullerenes 10 (and 5) Years Later*; Andreoni, W., Ed.; Kluwer: Dordrecht, The Netherlands, 1996; pp 437–457.
- (14) Dunlap, B. I. Constraints on small graphitic helices. *Phys. Rev. B* **1994**, *50*, 8134–8137.
- (15) Iijima, S.; Ichihashi, T.; Ando, Y. Pentagons, heptagons and negative curvature in graphite microtubule growth. *Nature* **1992**, *356*, 776–778.
- (16) Ihara, S.; Itoh, S. Molecular dynamics study of toroidal and helically coiled forms of graphitic carbon. *Surf. Rev. Lett.* **1996**, *3*, 827–834.
- (17) Terrones, H.; Terrones, M.; The transformation of polyhedral particles into graphitic onions. *J. Phys. Chem. Solids* **1997**, *58*, 1789–1796.
- (18) Crespi, V. H.; Benedict, L. X.; Cohen, M. L.; Louie, S. G. Prediction of a pure-carbon covalent metal. *Phys. Rev. B* **1996**, *53*, R13303–R13305.
- (19) O'Keefe, M.; Hyde, B. G. *Crystal Structures*; Mineralogical Society of America: Washington, DC, 1996.
- (20) Brinkmann, G.; Deza, M. Tables of face-regular polyhedra. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 530–541.
- (21) Grünbaum, B.; Shephard, G. C. *Tilings and Patterns*; Freeman: New York, 1985.
- (22) Stone, A. J.; Wales, D. J. Theoretical studies of icosahedral C₆₀ and some related species. *Chem. Phys. Lett.* **1986**, *128*, 501–503.
- (23) Kirby, E. C. On toroidal azulenoids and other shapes of fullerene cage. *Fullerene Sci. Technol.* **1994**, *2*, 395–404.
- (24) Fowler, P. W.; Cremona, J. E.; Steer, J. I. Systematics of bonding in nonicosahedral carbon clusters. *Theor. Chim. Acta* **1988**, *73*, 1–26.
- (25) Sah, C. H. A generalized leapfrog for fullerene structures. *Fullerene Sci. Technol.* **1994**, *2*, 445–458.
- (26) Brinkmann, G.; Dress, A. W. M. Phantasmagorical fullerenoids. *MATCH* **1996**, *33*, 87–100.
- (27) Grünbaum, B.; Löckenhoff, H. D.; Shephard, H. D.; Temesvari, A. H. The enumeration of normal 2-homeohedral tilings. *Geom. Dedicata* **1985**, *19*, 109–174.
- (28) Deza, M.; Shtogrin, M. Uniform partitions of 3-space, their relatives and embedding. *Eur. J. Combinatorics* in press.
- (29) Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *Physical properties of carbon nanotubes*; Imperial College Press: London, 1998.
- (30) Klein, D. J. Elemental benzenoids. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 453–459.
- (31) Deza, M.; Fowler, P. W.; Rassat, A.; Rogers, K. M. Fullerenes as tilings of surfaces. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 550–558.
- (32) Deza, M.; Shtogrin, M. Three, four- and five-dimensional fullerenes. *Southeast Asian Bull. Math.* **1999**, *23*, 9–18.
- (33) Stillwell, J. *Geometry of Surfaces*; Springer-Verlag: New York, 1992.

CI000010J