Addition Patterns in Carbon Allotropes: Independence Numbers and *d*-Codes in the Klein and Related Graphs

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The problem of predicting stoichiometries and patterns of chemical addition to a carbon framework, subject solely to the restriction that each addend excludes neighboring sites up to some distance *d*, is equivalent to determination of *d*-codes of a graph, and for $d = 2$ to determination of maximum independent sets. Sizes, symmetries, and numbers of *d*-codes are found for the all-heptagon Klein graph (prototype for "plumber's nightmare" carbon) and for three related graphs. The independence number of the Klein graph is 23, which increases to 24 for a related, but sterically relaxed, all-heptagon network with the same number of vertices and modified adjacencies. Expansion of the Klein graph and its relaxed analogue by insertion of hexagonal faces to form leapfrog graphs also allows all heptagons to achieve their maximum of 3 addends. Consideration of the π system that is the complement of the addition pattern imposes a closed-shell requirement on the adjacency spectrum, which typically reduces the size of acceptable independent sets. The *closed-shell* independence numbers of the Klein graph and its relaxed analogue are 18 and 20, respectively.

1. INTRODUCTION

Independence numbers and *d*-codes have proved be useful concepts in fullerene chemistry, as their definition lends itself naturally to the combinatorial description of chemical addition to a framework under steric constraints.[1−4] In particular, they place bounds on the maximum degree of addition of bulky functional groups. The independence number of a graph is the maximum size of an independent subset of graph vertices, i.e., a set such that no two of its members are neighbors.[5] Generalizing this concept, a *d*-code in a graph[6] is a subset of vertices such that all pairwise distances within the set are $\geq d$. Usually, it is only the largest *d*-codes for given *d* that are of interest. A *d*-code is a model for the chemical situation where a ligand casts a steric shadow that precludes addition to all vertices at distances $\leq d-1$. For all *d*-codes the concept of the independence number is central: the size $|C_2|$ of the largest *2*-code is the independence number of the graph, and the sizes $|C_d|$ of *d*-codes with $d > 2$ can be seen as independence numbers of augmented graphs in which new edges have been added for all pairwise separations $< d$.

The present paper deals with the application of these ideas to addition patterns on the hypothetical "carbon-foam" (Schwarzite) modifications of graphite.[7−9] These structures can be derived formally from decorations of minimal surfaces with trivalent carbon networks,[10,11] and their prototype is the covering of the "plumber's nightmare" *P* surface with heptagons. The most symmetrical finite analogue of this infinite all-heptagon network is the Klein map,[12,13] which has 56 vertices, 24 heptagonal faces, and is of genus 3. Glued according to Klein's original prescription, the derived periodic structure incorporates a degree of steric strain unacceptable in a carbon framework, but it is possible to design a chemically more plausible "untwisted" analogue by modifying the gluing rules.[13] Strain can also be lessened by inflation of the framework with hexagons between heptagonal faces, which yields structures that are also more plausible on electronic structure grounds. In the following sections, we therefore characterize the *d*-codes for the Klein graph, its untwisted analogue, and the inflated forms produced by the leapfrog transformation, using this mathematical data to provide models for chemical addition to carbon-foam variants of graphite.

The plan of the paper is as follows: the use of the independence number and a summary of the methods of determination of independent patterns and their application to the addition chemistry of C_{60} are outlined in §2. The properties of the Klein graph and the calculation of its independence-related properties are listed in §3 and §4. In §5 we describe how to lessen strain by untwisting the Klein graph, and finally in §6 we show that diluting the structure with hexagons to form a leapfrog, which reduces the strain even further, leads to structures with maximum independence numbers.

2. INDEPENDENCE AND THE ADDITION REGIOCHEMISTRY OF C_{60}

Before applying methods based on graph-theoretical independence to the case of the Klein graph and related mathematical objects connected to carbon foams, it may be useful to review the application of these ideas to the addition chemistry of C_{60}. The end product of bromination of [60]-fullerene is dominated by a single isomer $C_{60}Br_{24}$, characterized by X-ray crystallography as one of the few known chemical structures that belongs to the T_h point symmetry

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group.[14] An argument based on independence, coupled to a simple idea from chemical bonding theory, proves to be sufficient to account *in detail* for the experimental observations.[1]

The first premise is that the bulky bromine atoms will occupy independent (i.e. nonadjacent) sites; as the independence number of the truncated icosahedron is 24, the stoichiometry of the end-point of the bromination process is thereby rationalized. $C_{60}Br_{24}$ is the most highly brominated molecule in which it is possible for all brominated sites on the fullerene to be independent of each other in this sense. Patterns of 24 independent sites are readily catalogued by a direct depth-first search of the patterns in which each pentagonal ring of C_{60} bears two brominated sites. Symmetry reduction is carried out by representing each addition pattern as a binary code with 0 = C, 1 = Br in some standard vertex numbering scheme for the C_{60} substrate, acted upon by the 120 operations of the I_h point group represented as permutations, to yield the distinct canonical sequences and their site symmetry groups. It is found[1] that there are 1085 distinct isomeric patterns $C_{60}Br_{24}$ that satisfy the nonadjacency of brominated (i.e. sp^3) sites, out of 300 436 595 453 640 distinct decorations of the truncated icosahedron with 24 addends, counted without regard to independence.[15]

A second argument narrows down the possibilities decisively. Each addition pattern is the complement of a graph consisting of the $60 - 24 = 36$ bare carbon centers which span an unsaturated π system (typically a set of disconnected components). For chemical stability, both thermodynamic and kinetic, each of these π islands should have a closed-shell configuration, with a sufficient number of bonding orbitals to accommodate the local electron count in double occupation, and with a nonzero gap below an empty nonbonding or antibonding orbital, thus avoiding radicals and energetically unlikely zwitterionic states. Necessarily, therefore, each π subsystem must consist of an even number of bare carbon centers, though further restrictions must be imposed to ensure that each even-sized subsystem has an adjacency spectrum with the requisite closed shell. Application of the closed-shell requirement to the 1085 independent addition patterns of $C_{60}Br_{24}$ is straightforward, as all but one of them contains at least one isolated unbrominated site, thereby automatically failing the closed-shell requirement. The sole remaining pattern has all its bare carbon sites arranged in pairs and hence passes the closed-shell test. Furthermore, this sole surviving candidate from the application of the steric and electronic tests has the T_h symmetry and the precise arrangement of bromine addends observed in the experimental product.[14] The combination of independence and closed-shell arguments, both essentially graph-theoretical in nature, is clearly a powerful one.

However, it will not always be possible to find a maximum independent set that satisfies the chemical requirement for a closed shell. The independence number may be odd and hence force radical character, as for C_{70} with $I = 29$, or it may happen that all maximum independent sets include bare-carbon subsystems of odd size, as for C_{76}.[3] The solution is to define a *closed-shell independence number*, I^-, as the maximum size of an independent set subject to the requirement that each component of the complement graph should have a closed-shell adjacency spectrum.

If it exists, I^- is clearly bounded from above by I

$$I^- \le I \tag{1}$$

The existence qualification is necessary, as in some cases I^- may not have a defined value. For example, the tetrahedron has $I = 1$, but both triangle and tetrahedron have open-shell adjacency spectra, $\{+2, -1, -1\}$ and $\{+3, -1, -1, -1\}$, respectively, so that I^- is neither 1 nor 0.

Another naive upper bound on I^- is readily found by considering the detailed construction of an isomer C_nX_m in which all m X addends are independent. Let the m vertices in the independent set be colored black and the $n-m$ vertices outside the independent set be colored white, and let a_r be the number of white vertices with exactly r black neighbors. Counting white vertices

$$a_0 + a_1 + a_2 + a_3 = n - m \tag{2}$$

and counting black-white contacts

$$0\,a_0 + 1\,a_1 + 2\,a_2 + 3\,a_3 = 3\,m \tag{3}$$

Since a_3 must vanish if the pattern is to avoid isolated (radicaloid) carbon centers, m, and hence the closed-shell independence number must satisfy

$$m = (2\,n - a_1 - 2\,a_0)/5 \tag{4}$$

leading to a second bound

$$I^- \le 2n/5 \tag{5}$$

with equality $I^- = 2n/5$ when $a_2 = n - m$ and $a_0 = a_1 = 0$, in which case all the bare carbon centers occur in localized double bonds. Sometimes (1) and sometimes (5) is the stricter bound. For example, the truncated dodecahedron has $I = 20 < 2n/5 = 24$, but the cube has $I = n/2 = 4 > 2n/5 = 3.2$ and $I^- = 2$. Icosahedral C_{60} satisfies $I = I^- = 2n/5 = 24$. A computer search of independent sets fixes I^- as 26, 28, 32 for isolated-pentagon C_{70}, C_{76} (T_d) and C_{84} (32 for both isomers 22 and 23), respectively, and gives, for example, 10 candidates for the end product of bromination of C_{70} under the nonadjacency rule.[3]

Higher d-codes have also been considered for C_{60} and C_{70},[2] and the sizes of the maximum independent sets at each distance obtained using a suitably augmented adjacency matrix as input to the Hansen and Mladenović program for finding stable sets.[16] For C_{60}, values of $d = 2$ to $d = 9$ lead to independent-set sizes $|C_d| = 24, 12, 7, 6, 3, 2, 2, 2$, and for C_{70}, values $d = 2$ to $d = 10$ lead to $|C_d| = 29, 15, 8, 6, 4, 3, 2, 2, 2$. Closed-shell codes have also been found for C_{60} and C_{70} at the various higher values of d, again giving small but complete sets of plausible candidates for sterically constrained addition products. At $d = 3$, for example, there are 9 independent and fully closed-shell addition patterns $C_{60}X_{12}$, and a further 3 that have open shells only through an accidental degeneracy at the simplest level of Hückel theory.[2]

The same techniques are now applied to some nonplanar graphs that may represent carbon foams.

3. THE KLEIN GRAPH

The Klein graph is a regular graph with exactly three edges meeting at every vertex, and its girth (smallest cycle length)

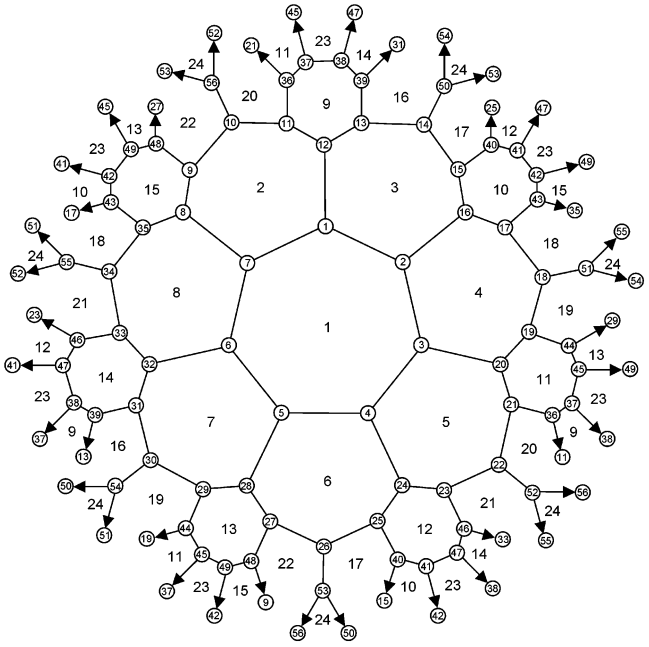

Figure 1. Schlegel-like diagram of the 56-vertex Klein map, viewed from a central heptagonal face.

is seven. In Figure 1, the adjacencies of the Klein graph are displayed in a modified Schlegel diagram, viewed from a heptagonal cycle to visualize the 7-fold symmetry. The graph has a highly degenerate adjacency spectrum, with eigenvalues (and multiplicities) $(3)^1$, $(1+\sqrt{2})^8$, $^1/_2(-1+\sqrt{17})^7$, $(\sqrt{2})^6$, $(0)^7$, $(1-\sqrt{2})^8$, $(-\sqrt{2})^6$, $(-2)^6$, $^1/_2(-1-\sqrt{17})^7$. Considered as an isolated Hückel π system, it therefore has an open-shell configuration, with 6 electrons in the 7-fold degenerate nonbonding level. Its complexity (number of spanning trees) is $2^{26} \times 3^7 \times 5^6 \times 7^5 = 38\,542\,412\,611\,584\,000\,000$, equal to 14/15 of the complexity of icosahedral C_{60}. One of the intriguing features of the Klein graph is its extremely high symmetry. A detailed analysis of the group theory of the Klein graph and its relevance to possible carbon allotropes of negative curvature is given in ref 13.

The full automorphism group of the graph has order 336. It contains a rotational subgroup of order 168, PSL(2,7), consisting of only even permutations. That group is isomorphic with the central quotient group of SL(2,7), being the special linear group of singular 2×2 matrices over the finite field F_7. As this group acts transitively on a set of 7 elements, all containing 8 vertices and bearing octahedral *O* symmetry, it will be denoted ^7O and called the heptakisoctahedral[13] group. It is clear from Figure 1 that the polyhedral graph also has reflection symmetry. Adding a reflection operation to the rotational subgroup ^7O as an extra generator leads to the parent group of order 336. This product group will be denoted as ^7O_d, as its construction is similar to the extension of rotation groups by dihedral symmetry planes. The 336-element group ^7O_d can be generated by a pair of elements consisting of a σ_v reflection operation and a nonincluded C_7 face-rotation (Table 1).

The 336 symmetry-elements are divided into 9 conjugacy classes: E, $21C_2$, $56C_3$, $42C_4$, $48C_7$, $28\sigma_v$, $56S_6$, $42S_8$, and $42S_8^3$. Note that ^7O_d does not belong to the family of point groups but is in fact a permutational group, so care must be taken with the use of symmetry operation names for the automorphisms. For instance, an operation such as σ_v shares

Table 1. A Pair of Generators for the Automorphism Group of the Klein Graph Expressed as Permutations of Vertices 1−56 in the Numbering Scheme of Figure 1

C_7	2	3	4	5	6	7	1	12	13	14	15	16	17	18
	19	20	21	22	23	24	25	26	27	28	29	30	31	32
	33	34	35	8	9	10	11	40	41	42	43	44	45	37
	36	46	47	48	49	39	38	51	52	53	54	55	56	50
σ_v	1	2	16	15	14	13	12	11	10	9	8	7	6	5
	4	3	20	19	18	17	43	42	41	40	25	26	53	50
	54	30	31	39	38	37	36	35	34	33	32	24	23	22
	21	51	55	47	46	56	52	28	44	49	27	29	45	48

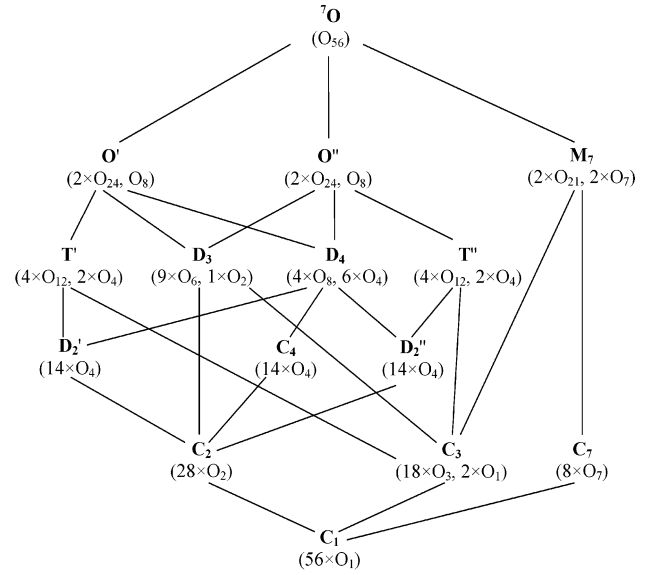

Figure 2. Genealogical tree of subgroups of the heptakisoctahedral group ^7O. Between brackets we denote the orbit structure of the Klein graph under the subgroup.

with reflection its cyclic nature and orientation-reversing character but cannot be identified with a crystallographic symmetry plane of the periodic lattice on which the polyhedron can be mapped. However, the terminology proves convenient for describing the different subgroups, which can themselves exhibit point group symmetry.

Replacement of the σ_v generator by a C_3 rotation about one vertex of the generating face or simple deletion of all improper operations leads to the rotational subgroup of index 2, comprising all 168 orientation-preserving elements, which will be denoted ^7O. The class structure is E, $21C_2$, $56C_3$, $42C_4$, $24C_7$, and $24C_7^3$, where the original class of 48 7-fold "rotations" is separated into two classes C_7 and C_7^3, each containing 24 elements. Figure 2 shows the genealogical tree of subgroups of ^7O, together with the orbit composition of the 56-vertex Klein graph under these subgroups. As the figure shows, all subgroups with the exception of one, the hemimetacyclic group M_7 of order 21, are point groups.

It can be shown that the lowest genus of a surface on which it is possible to embed the Klein graph as a map without forced edge crossings is $g = 3$ (a sphere with three handles, a triple torus).[17] In such a mapping all 24 smallest cycles are realized as heptagonal faces. The full automorphism group is retained in the map; it has order 336 and acts transitively on the vertices, edges, and faces, to form a regular map with all faces of the same heptagonal form and all vertices at the meeting point of 3 heptagons. Such a regular map can therefore be seen as an analogue of the spherical platonic solids. To form an infinitely extended system

corresponding to a 3D carbon foam, the isolated-molecule unit of the 56-vertex Klein graph must be embedded on a minimal surface consisting of genus 3 subunits. The prototypical example is the plumber's nightmare surface *P*, which will be used for all 3D realizations in the present work. Figure 3 gives an embedding of the Klein graph onto *P*. The underlying surface has full octahedral O_h symmetry, but the map itself has only the rotational symmetry *O* and hence has enantiomeric left and right-handed spatial realizations.

4. *d*-CODES OF THE KLEIN GRAPH

The Klein graph has diameter 6 and as its automorphism group acts transitively on the vertices, all 56 of them belong to the same orbit and have 3, 6, 12, 15, 18, and 1 neighbors at distances 1, 2, 3, 4, 5, and 6, respectively. The sizes $|C_d|$ of the *d*-codes ($2 \le d \le 7$) can be found using the standard approach for calculation of independence number described in §2 and applying it to a series of graphs generated from the Klein graph by successive addition of edges for distances $d-1$. The independence number of the Klein graph, $I = |C_2|$, is found to be 23, i.e., one less than the bound of 24 obtained by supposing that every one of the heptagons reaches its maximum quota of 3 black vertices (i.e. vertices in the independent set). It is straightforward to show that the maximum-quota assumption leads to a contradiction, so 24 is not achievable.

In a set of 23 independent vertices of a graph with 24 heptagonal faces, there must be some "defective" heptagons that have less than the maximum three black vertices. Denoting by h_i the number of heptagons containing *i* black vertices, we have, from the total number of faces

$$\sum_{i=0}^{3} h_i = 24 \tag{6}$$

and, from the number of black vertices, each appearing in three heptagons,

$$\sum_{i=0}^{3} i h_i = 69 \tag{7}$$

Any solution set $\{h_i\}$ is one of three types $\{h_3, h_2, h_1, h_0\} = \{21, 3, 0, 0\}$, $\{22, 1, 1, 0\}$, $\{23, 0, 0, 1\}$. The second and third solutions are easily excluded by recalculating the independence number for the Klein graph in which a heptagon with either no black vertices or one black vertex has been planted. In both cases the independence number of the modified graph falls below 23. A further simplification comes from the fact that the two black vertices in each of the three defective heptagons must be next nearest neighbors (the alternative configuration of black-white-white-black in which they would be third neighbors is again excluded by computation for a graph with a "planted" heptagon of this type).

The results for $|C_d|$ for all *d* are given in Table 2 together with the total numbers of codes. Representation of symmetry operations as vertex permutations can be used to project out the unique symmetry-distinct codes from the full set of N_d. Table 3 lists the numbers of symmetry-distinct *d*-codes and their site symmetries under the operations of the full group ^7O_d, the rotational subgroup ^7O, and the octahedral subgroup

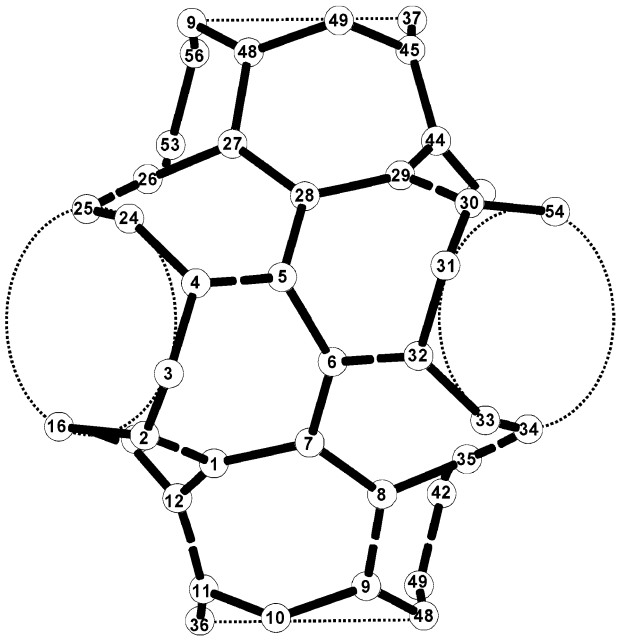

Figure 3. Decoration of the plumber's nightmare surface with the Klein graph, using the numbering of Figure 1.

Table 2. *d*-Codes on the Klein Graph[a]

d	2	3	4	5	6	7
$\|C_d\|$	23	12	7	4	2	1
N_d	2744	728	16	84	28	56

[a] $|C_d|$ is the size of the code and N_d, the number of ways an independent set of size $|C_d|$ can be constructed, without regard to symmetry.

O, the symmetry of the 3D realization on the plumber's nightmare. The table also lists the graphs that characterize the contact relationships within the various *d*-codes: the contact graphs. A contact graph for a given *d*-code has $|C_d|$ vertices connected by edges for each pairwise distance *d*. The codes for $d = 7, 6, 5, 4$ all yield contact graphs that are complete graphs of dimension $|C_d|$, i.e., K_7, K_4, K_2, and K_1. All graphs at $d = 5$ yield the tetrahedral K_4. The contact graphs at $d = 3$ and $d = 2$ are more complicated: for $d = 3$, the five distinct ^7O_d codes span different graphs with 25 or 27 edges; for $d = 2$ the 11 distinct ^7O_d codes span 11 graphs, all with 45 edges.

The chemical interest of the independence problem lies in the closed-shell independence numbers, I^-. In a search for I^- of any graph, solutions where the 2-code is of odd size can be excluded automatically because they cannot lead to closed shells. The closed-shell independence number of the Klein graph therefore, in contrast to I^- for C_{60}, cannot reach the independence number i.e., 23. Equation 5 gives an upper bound for I^- of 22. There are 188 608 codes of this size, reduced to 517 symmetry-distinct cases under the operations of ^7O_d. A simple check for isolated white vertices is sufficient to exclude all 517 as they all give open shells. Of the 29 927 828 possibilities for 2-codes of size 20, 1708 have no isolated vertices, and, of these, 7 are distinct by symmetry. Again, all 7 can be excluded because they have at least one path of length three as a subgraph, with spectrum $\{\pm\sqrt{2},0\}$ and a local open shell. The search moves on to 2-codes of size 18: raw counting gives 637 745 080 solutions, 3 275 916 of which remain after removal of those with

Table 3. Symmetry-Distinct *d*-Codes for the Klein Graph under the Operations of ^7O_d, ^7O, and O, Respectively[a]

d	2	3	4	5	6	7
G	(45 edges)	(25/27 edges)	K_7	K_4	K_2	K_1
$N_d(^7O_d)$	11	5	1	2	1	1
	$1(C_{3v})$, $3(C_3)$, $7(C_1)$	$1(D_3)$, $2(C_S)$, $2(C_2)$	$1(M_7)$	$1(T)$, $1(C_{3v})$	$1(D_{3d})$	$1(C_{3v})$
$N_d(^7O)$	21	8	2	3	1	1
	$7(C_3)$, $14(C_1)$	$2(D_3)$, $4(C_2)$, $2(C_1)$	$2(M_7)$	$2(T)$, $1(C_3)$	$1(D_3)$	$1(C_3)$
$N_d(O)$	119	40	2	7	3	3
	$7(C_3)$, $112(C_1)$	$2(D_3)$, $16(C_2)$, $22(C_1)$	$2(C_3)$	$1(T)$, $1(D_2)$, $2(C_3)$, $1(C_2)$, $2(C_1)$	$1(D_3)$, $2(C_2)$	$1(C_3)$, $2(C_1)$

[a] *G* is the contact graph formed by connecting all vertices of a *d*-code at distance $d-1$.

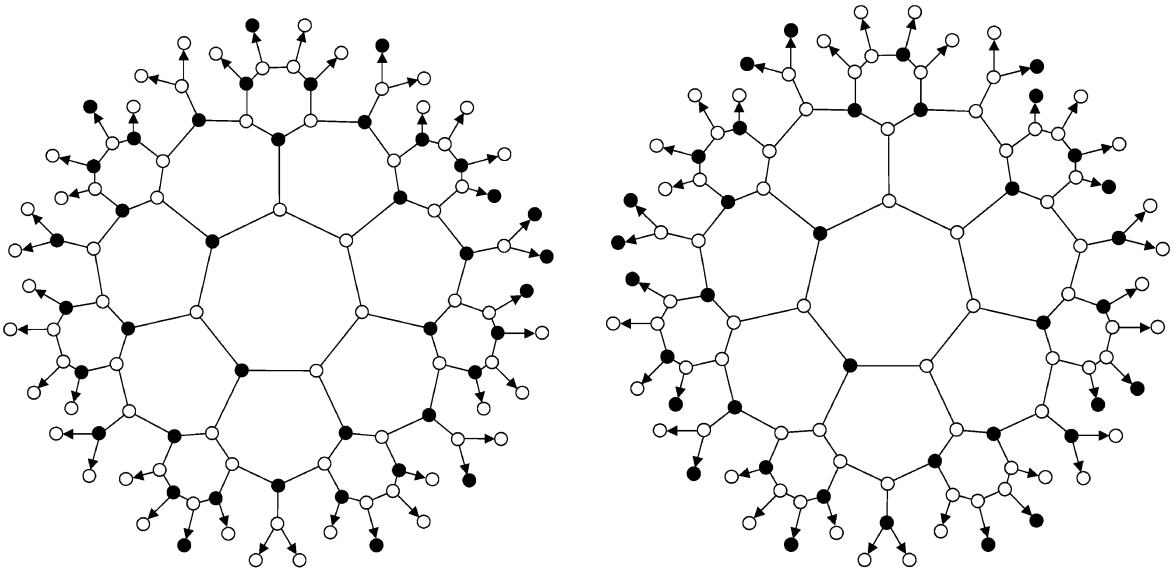

Figure 4. (Left) The maximum independent set ($I = 23$), with C_{3v} symmetry. (Right) The unique maximal closed-shell set ($I^- = 18$), with only even paths as subgraphs in the complement. For clarity, vertex labels are omitted.

isolated white vertices. Symmetry reduction of these leads to 9798 distinct isomers of which 1915 have no path of length three as a subgraph. Explicit calculation of the π-subgraph decomposition of each of these isomers and a check of the spectrum identify just 20 closed-shell isomers, all having the trivial symmetry C_1. Thus I^- for the Klein graph is 18.

Of the 20 solutions, one stands out as its complement is composed of paths of even length (see Figure 4); all other solutions have at least one subgraph that is branched or contains a cycle. In Table 4 we list the π-subgraph decomposition for all 20 solutions. P_x denotes a path of length *x*; the other closed-shell subgraphs are depicted in Figure 5.

5. THE UNTWISTED EMBEDDING: THE PSEUDO-KLEIN MAP

Although the Klein graph is of great mathematical beauty and high symmetry, a minimal surface composed of Klein subunits embedded on the plumber's nightmare leads to a twisted structure which introduces an unacceptable strain for its realization as a carbon network.[13] This is illustrated in Figure 3, where it can be seen that, to superimpose identically labeled vertices, one has to twist the tubes back through an angle of 90° before gluing them together. All three tubes are surrounded by paths of four heptagons and are bordered by an 8-cycle of which four vertices make a connection to the next subunit. A tube can therefore be twisted through an angle of −90°, 0°, 90°, or 180° before it is glued to the next unit. Combining the allowed twists leads to $4^3 = 64$ maps, not necessarily distinct, all with genus 3 and all consisting of 24 heptagonal faces.

Table 4. Subgraph Decomposition of the 20 Closed-Shell Solutions of Size 18 for the Klein Graph[a]

	size																			
	2	4	6		8			10			12							14		
	P_2	P_4	P_6	a	P_8	b	c	P_{10}	d	e	f	g	h	i	j	k	l	m	n
1	2	2	3	.	.	.	1	.	.	.	.	.	.	.	.	.	.	.	.	.
2	5	.	.	.	2	.	.	.	.	.	.	.	1	.	.	.	.	.	.	.
3	5	2	.	.	1	.	.	.	.	.	.	.	.	.	.	1	.	.	.	.
4	2	3	2	.	.	.	.	.	.	1	.	.	.	.	.	.	.	.	.	.
5	4	1	1	.	1	.	.	.	.	.	.	.	1	.	.	.	.	.	.	.
6	2	4	1	.	.	.	.	.	.	.	.	.	.	.	1	.	.	.	.	.
7	3	2	2	.	.	.	.	.	.	.	.	.	.	1	.	.	.	.	.	.
8	1	4	2	.	.	1	.	.	.	.	.	.	.	.	.	.	.	.	.	.
9	1	4	2	.	.	1	.	.	.	.	.	.	.	.	.	.	.	.	.	.
10	3	2	1	.	1	.	.	.	1	.	.	.	.	.	.	.	.	.	.	.
11	3	3	1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	1	.
12	2	4	1	.	.	.	.	.	.	.	.	1	.	.	.	.	.	.	.	.
13	2	3	1	.	1	1	.	.	.	.	.	.	.	.	.	.	.	.	.	.
14	3	3	1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	1	.	.
15	3	1	1	1	2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
16	3	2	.	1	1	.	.	1	.	.	.	.	.	.	.	.	.	.	.	.
17	5	.	.	.	2	.	.	.	.	.	1	.	.	.	.	.	.	.	.	.
18	4	1	.	.	1	1	.	1	.	.	.	.	.	.	.	.	.	.	.	.
19	1	4	2	.	1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
20	2	5	.	.	.	.	.	.	.	.	.	.	.	.	.	.	1	.	.	.

[a] P_x stands for the even path of length *x*. The other possible subgraphs (a−n) are listed in Figure 4. Each row shows how the 38 white vertices of the graph, i.e., the bare carbon atoms when the *d*-code represents an addition pattern in which black vertices are occupied by attached groups, are partitioned into isolated π systems.

Clearly, the graphs corresponding to the finite analogues of these newly formed embeddings will not be isomorphic to the Klein graph. Their adjacencies can be derived from

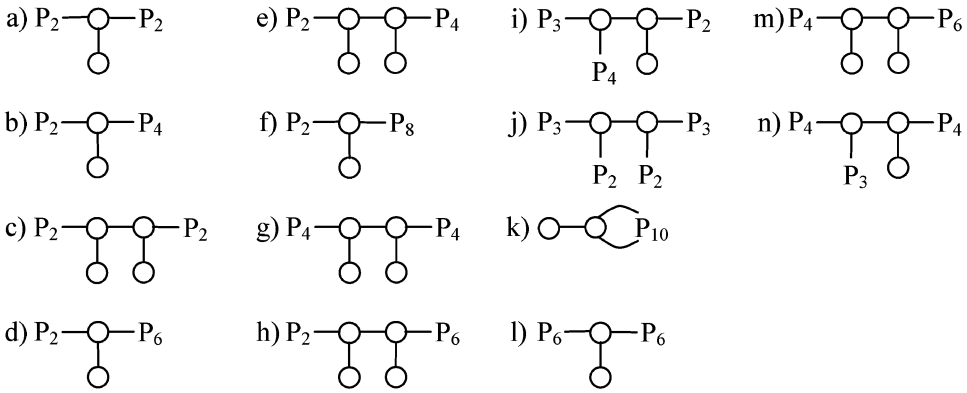

Figure 5. Subgraphs appearing in the 20 closed-shell solutions of size 18 for the Klein graph.

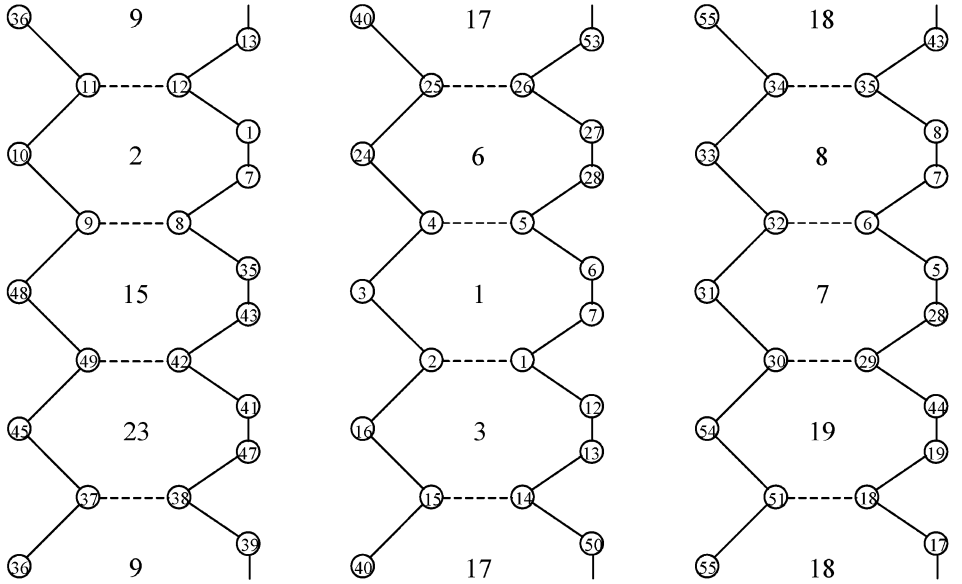

Figure 6. Local environment of the four edges broken and remade in the construction of Klein-like maps. The illustrated configuration corresponds to tubes of the Klein graph itself embedded on the plumber's nightmare.

those of the Klein graph by breaking 12 connections (indicated by dashed lines in Figure 3) and restoring them after the chosen twist has been applied. Figure 6 shows the local environment of the edges that have to be broken. The configuration shown corresponds to that of the original Klein graph, for which the twist is $-90°$. In the figure, breaking four edges in one tube, and moving the right-hand stack of vertices down by one step leads to a gluing of that tube without twisting. Movement by 2 or 3 steps leads to twists of 90° and 180°, respectively. With four local twists, and three tubes, there are 64 possible cases, which reduce by permutational symmetry of the gluing rules over the tubes to 20 graphs; it turns out that two of the graphs are isomorphic, reducing the final list of distinct twisted embeddings to 19. The extra isomorphism arises between the graph where two tubes are given a Klein twist and one is given no twist, and the graph where two tubes also have a Klein twist but the third is twisted through 180°.

Of particular chemical interest is the object formed by gluing all three tubes together without a twist, producing the least strained all-heptagon network. We will call this graph the pseudo-Klein graph, and its embedding on the plumber's nightmare the *pseudo-Klein* map. We repeat the calculations made previously for the Klein graph for this untwisted analogue, for which the *d*-code sizes may now differ because of the changes in adjacencies. On untwisting the tubes, the ${}^7O_d$ symmetry of the Klein graph is lost and is reduced to *O*, which is still compatible with that of the underlying surface. In Figure 7 we show the adjacencies of the untwisted form. Because of the loss of 7-fold symmetry, the diagram is no longer viewed from a heptagonal face but is drawn around a vertex on one of the octahedral 3-fold axes. The numbering of faces is matched to that in Figure 1: the 12 faces that remain in place after untwisting retain their numbering; the other 12 form the 4-heptagon cycles that bound the three tubes and are indicated by dashed arcs. This graph has an adjacency spectrum that includes an accidentally 4-fold degenerate zero. In the spectrum, the eigenvalues $(3)^1$, $(1+\sqrt{2})^2$, $^1/_2(-1+\sqrt{17})^1$, $(\sqrt{2})^3$, $(0)^4$, $(1-\sqrt{2})^2$, $(-\sqrt{2})^3$, $^1/_2(-1-\sqrt{17})^1$ survive from the Klein graph; together with $(2)^3$, and 12 other triply degenerate eigenvalues (5 positive, 7 negative) they make up the set of 56. Considered as an isolated Hückel π system, the pseudo-Klein graph therefore has an open-shell configuration, again with 6 electrons in the 4-fold degenerate nonbonding level. The complexity of the pseudo-Klein graph is $2^{14} \times 3^4 \times 7^2 \times 3^{13} \times 269^3 = 37\,708\,821\,494\,943\,105\,024$, i.e., smaller than that of the Klein graph by some 2%.

Table 5 lists, for the pseudo-Klein map, the *d*-codes, the number of solutions N_d, and their symmetries under the

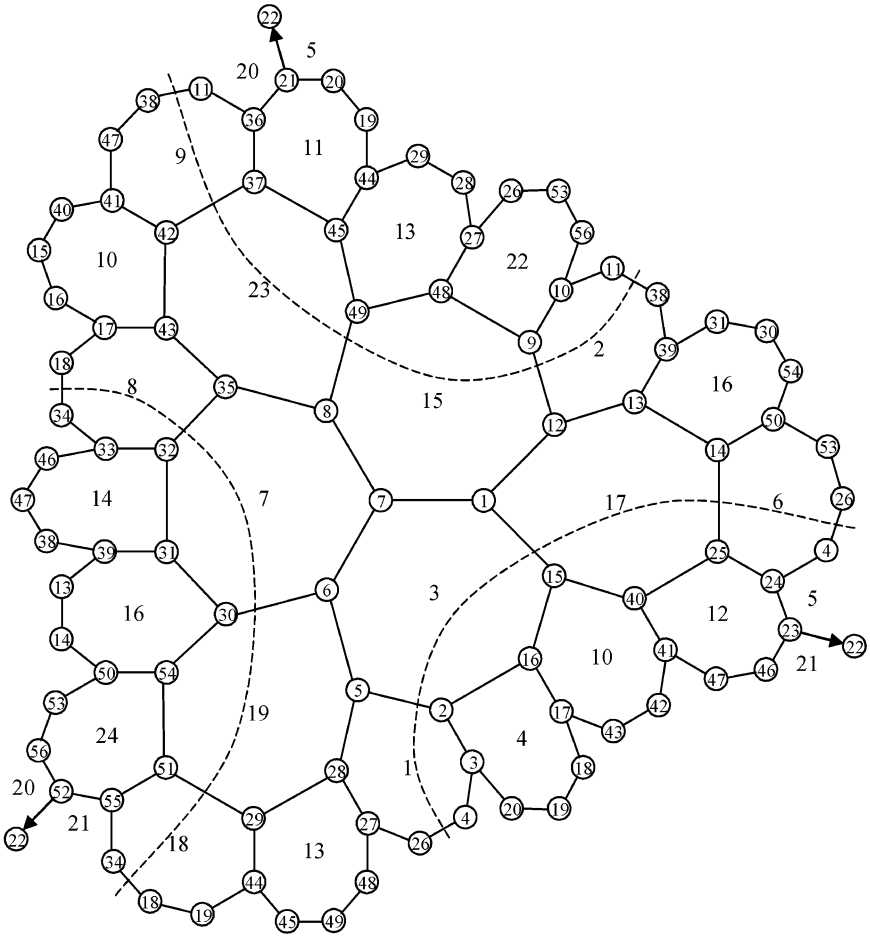

Figure 7. Schlegel-like diagram of the 56-vertex pseudo-Klein map viewed from a point on one of the 3-fold axes.

Table 5. *d*-Codes and Symmetry-Distinct *d*-Codes for the Pseudo-Klein Graph under the Symmetry Operations of *O*

d	2	3	4	5	6	7	8
$\|C_d\|$	24	12	7	4	2	2	1
N_d	8	604	8	138	76	4	56
	1	33	1	8	5	1	3
$N_d(O)$	(C_3)	20(C_1), 8(C_2), 3(C_4), 1(D_2), 1(D_3)	(C_3)	5(C_1), 2(C_3), 1(T)	2(C_1), 2(C_2), 1(D_3)	(D_3)	2(C_1), 1(C_3)

operations of *O*. These results show several differences from the Klein graph. First, untwisting increases the diameter of the graph from 6 to 7. The 7-codes in the pseudo-Klein map are of size 2; there are only 4 solutions, because under symmetry *O*, the vertices fall into three orbits, of length 8, 24, and 24, respectively (see Figure 3). A first orbit contains all eight vertices positioned on one of the 3-fold axes, with C_3 site symmetry and consists of the 4 antipodal pairs that form the 7-code solutions. A second orbit, with C_1 symmetry, consists of the 24 nearest neighbors of vertices in the first orbit. A third orbit, again with C_1 symmetry, consists of the remaining 24 vertices, in 8-cycles bounding the tubes. The three orbits give rise to the symmetry-distinct 8-codes.

An intriguing fact is that the removal of the tube twist leads to an increase of the independence number from 23 to 24 and thus allows a solution in which all 24 heptagons obtain their maximum quota of three vertices. Thus, as a carbon framework, the pseudo-Klein map is both sterically relaxed and more accommodating of large addends. In fact, among the 19 different twisted/untwisted versions of the Klein map, there are exactly four that have this increased independence number of 24: they are the graphs in which each tube has either no twist or a twist of 180°. The presence of any tube twist of ±90° leads back to an independence number of 23.

It would be unfeasibly expensive to find all possible $I = 24$ solutions by brute force. We therefore use an approach with planted local configurations. Under the *O* symmetry of the pseudo-Klein graph, all faces remain equivalent, so we can begin by giving one face its starting configuration of 3 black vertices, which is equivalent to deciding where the neighboring pair of white vertices is planted. This pair can be planted in four nonequivalent positions, depicted in Figure 8 together with an indication of the orbits of *O* to which the vertices belong, which shows that the pair of white neighbor vertices can be 1−2, 2−2, 2−3, or 3−3. Recalculation of the independence number with a planted heptagon in each configuration excludes the 2−2 combination, in which the neighboring white vertices occupy the two next neighbor orbit-2 vertices. Although all other starting configurations lead to solutions, they all condense to the same C_3 isomer after symmetry reduction. In Figure 9 (left) we show this unique solution.

Various contact graphs appear among the *d*-codes summarized by Table 5. A unique C_3 solution also appears among the 4-codes, illustrated in Figure 9 (right), but unlike the 4-code of the Klein map, its contact graph is not K_7; for $d = 5$, the contact graphs are K_4 tetrahedra apart from one C_1 case, where the contact graph is a "butterfly", i.e., a

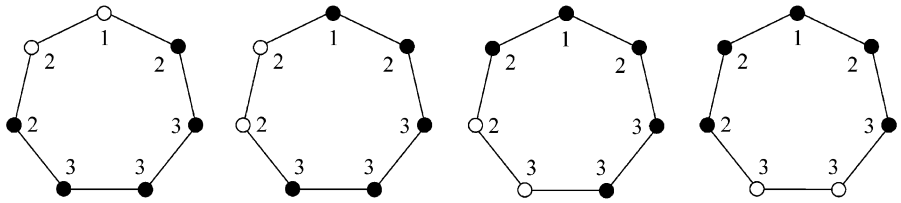

Figure 8. Indication of the orbit-structure of the vertices of a heptagonal face in the pseudo-Klein map. A white vertex pair can be planted in 4 nonequivalent ways.

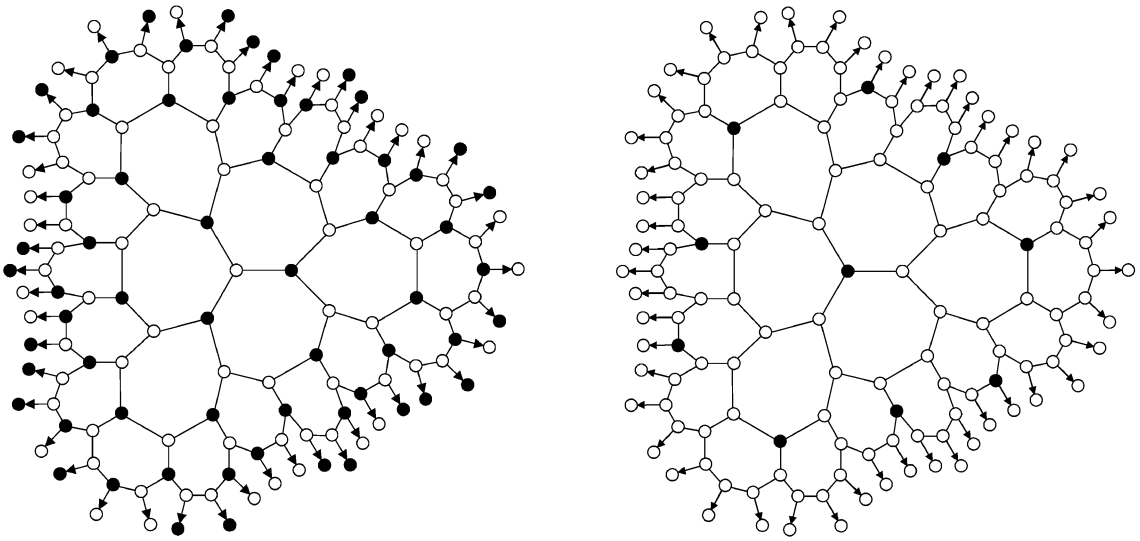

Figure 9. Unique $d = 2$, $I = 24$ and $d = 4$, $I = 7$ codes for the pseudo-Klein map. Numbering as in Figure 7.

tetrahedron with one open edge; for $d = 6$, the contact graphs are all K_2 dimers, with the exception of the D_3-symmetric pair of vertices that form both a 6-code and the unique 7-code.

The maximum independent sets are not themselves of direct chemical relevance because they all contain isolated vertices, as seen from eq 5. For independent sets of size 22, one finds 178 492 solutions, all containing at least one isolated vertex. There are 28 964 138 solutions of size 20, of which 856 (41 symmetry-distinct in O) contain no isolated vertex. Of these, three solutions are without paths of length three, and only one survives a check for closed shells; it consists of six paths of length four and six of length two (Figure 10). On untwisting the tubes, the independence number has therefore increased from 23 to 24, and the closed-shell-independence number from 18 to 20. For the pseudo-Klein graph, both maximum independent and maximum closed-shell independent sets are unique.

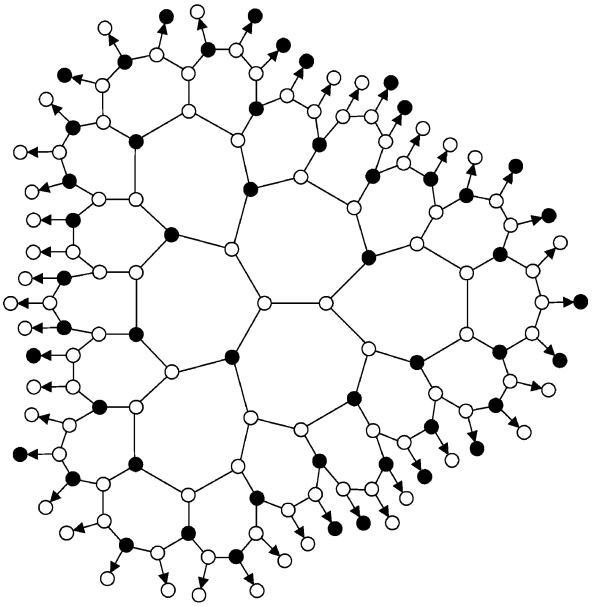

Figure 10. The unique $I^- = 20$ closed-shell solution for the pseudo-Klein map.

6. LEAPFROGS OF KLEIN AND PSEUDO-KLEIN MAPS

In the previous section we described how untwisting the tubes of the Klein graph would lead to a relaxation of strain in the all-heptagon network. A second, and probably better, way is by dilution of the all-heptagon network with hexagons, thus distributing the strain over a larger number of atoms. In the present section, the d-codes of the leapfrogs of the Klein and pseudo-Klein maps are investigated.

The *leapfrog* transformation[18] of a polyhedron P is obtained by performing two consecutive transformations: first, all faces are capped, and then the dual is taken. This results in a polyhedron $L(P)$ with three times as many vertices as the original, but with the same initial topology. After such a leapfrog transformation, all initial faces will be completely surrounded with hexagons. For both Klein and pseudo-Klein maps, this transformation leads to 168-vertex polyhedra with 24 disjoint heptagons, separated by 56 hexagons.

The independence number turns out to be 72 in both cases, therefore leading to isomers in which all heptagons realize their maximum of three vertices. The set of d-code sizes is shown in Table 6 and follows the same trend as for the parent

Table 6. *d*-Codes for the Leapfrogs of the Klein Map and Its Untwisted Analogue

d	2	3	4	5	6	7	8	9	10	11	12
L(Klein)	72	39	21	13	8	6	4	3	3	1	1
L(pseudo-Klein)	72	39	22	14	9	7	4	4	2	2	1

Table 7. Symmetry Distinct Independent Sets of the Leapfrogs of the Klein Graph and Its Untwisted Form

	C_1	C_2/C_2'	C_3	C_4	D_2'	D_3	T	S_8
L(Klein)								
$N_d(^7O_d)$	28 949 924	419	981	6		1	1	4
$N_d(^7O)$	57 899 848	838	1962	16		2	2	
$N_d(O)$	405 309 070	840/1695	1963	16	1	2	1	
L(pseudo-Klein)								
$N_d(^7O_d)$	346 926 912	1483/819	1972	19	1	1	1	

maps, namely that for a given *d*, the *d*-code in the pseudo-Klein untwisted map is greater or equal to the Klein case. The *d*-codes were easily calculated for all cases except when *d* was equal to three or four. In these two cases it was necessary to assist the algorithm by planting some initial configurations.

A calculation of all possible maximum independent sets was performed by an enumeration algorithm similar to that used for C_{60}, where now the 12 pentagons are replaced by the 24 heptagons of the Klein-leapfrog and pseudo-Klein-leapfrog, which cover all vertices of the 168-vertex graphs. The algorithm performs a depth-first search on a tree containing 7^{24} nodes, which in itself would be unfeasible if most of the routes in the upper levels of the tree did not produce early contradictions and close off many of the branches.

The total number of solutions for $d = 2$ is 9 727 355 484 for the leapfrog of the Klein map and 8 326 289 414 for the leapfrog of the pseudo-Klein map. Reduction to symmetry-distinct solutions was carried out by checking for identity of the solution and its image under one representative operation of each conjugacy class of the group, i.e., calculating the permutation character of the isomer set and storing the non-C_1 isomers. Most have only the trivial C_1 symmetry. In a final step we remove the duplicates from the list and derive the symmetry of the remaining solutions, which are listed in Table 7.

7. CONCLUSIONS

Independent sets, sizes, symmetries, and numbers of *d*-codes have been found for the all-heptagon Klein graph, which is the highly prototype for plumber's nightmare carbon foams, in which networks of carbon atoms might cover infinite surface of genus 3, and for three related graphs. This mathematical problem is translated directly into the problem of predicting stoichiometries and patterns of chemical addition to a carbon framework, subject solely to the restriction that each addend excludes neighboring sites up to some distance *d*. The study has shown some significant differences between the fullerenes and these analogues of higher genus. Unlike the protypical all-pentagon spherical fullerene (C_{20}), the Klein map does not have a maximum independent set in which all faces achieve their individual independence numbers. In icosahedral C_{20}, independent sets exist in which each pentagonal face contains two members of the set, and the independence number of the whole graph is therefore 8; in the Klein C_{56} graph, at most 21 heptagons contain three members of the set, and the independence number of the graph is 23, one short of the maximum 24 that would require all heptagons to contain the full quota of three members of the set. Unlike the C_{20} fullerene, the Klein map, considered as a molecular unit has a closed-shell independence number that is lower than its independence number − in this case by 5. A point of similarity with the fullerenes is that a graph where all $(2r+1)$-sized rings achieve their full quota of r members of the independent set is achieved by the leapfrog transformation; the independence number is 24 for the smallest leapfrog fullerene (icosahedral C_{60}) and 72 for the leapfrog of the Klein graph. However, while the fullerene has equality of independence and closed-shell independence numbers, the leapfrog Klein map does not. The closed-shell independence number for the leapfrog of the Klein map has not been computed, but it is smaller than the independence number by at least 6.

An important difficulty with the literal use of the Klein graph as a building block for carbon foam allotropes is the considerable steric strain shown by the Klein map and its derivatives on the plumber's nightmare surface. A related graph in which this twisting strain has been removed is chemically much more plausible, and its properties have been studied here in parallel with those of the Klein map. The untwisted pseudo-Klein map achieves the independence number of 24 and has the higher closed-shell independence number of 20, suggesting that the derived carbon foam would be able to accommodate a higher degree of coverage by bulky addend atoms. Both maximum independent and maximum closed-shell independent coverings of this map are unique and have local C_3 symmetry.

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