Structure and Properties of the Nonface-Spiral Fullerenes \( T-C_{380} \), \( D_3-C_{384} \), \( D_3-C_{440} \), and \( D_3-C_{672} \) and Their Halma and Leapfrog Transforms

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ABSTRACT: The structure and properties of the three smallest nonface-spiral (NS) fullerenes \( NS-T-C_{380} \), \( NS-D_3-C_{384} \), \( NS-D_3-C_{440} \) and the first isolated pentagon NS-fullerene, \( NS-D_3-C_{672} \), are investigated in detail. They are constructed by either a generalized face-spiral algorithm or by vertex insertions followed by a force-field optimization using the recently introduced program fullerene. The obtained structures were then further optimized at the density functional level of theory and their stability analyzed with reference to \( I_5-C_{60} \). The large number of hexagons results in a higher stability of the NS-fullerenes compared to \( C_{60} \), but, as expected, in a lower stability than most stable isomers. None of the many investigated halma transforms on nonspiral fullerenes, \( NS-T-C_{380} \), \( NS-D_3-C_{384} \), \( NS-D_3-C_{440} \), and \( NS-D_3-C_{672} \) admit any spirals, and we conjecture that all halma transforms of NS-fullerenes belong to the class of NS-fullerenes. A similar result was found not to hold for the related leapfrog transformation. We also show that the first known NS-fullerene with isolated pentagons, \( NS-D_3-C_{672} \), is a halma transform of \( D_3-C_{168} \).

INTRODUCTION

Fullerenes have exactly 12 pentagons, and the location of the pentagons within the network of hexagons uniquely determines the fullerene structure. A convenient way to characterize fullerenes is by using the face-spiral algorithm by Manolopoulos and Fowler (MF).1,2 This algorithm spirally unwinds (clockwise or anti-clockwise) the faces of a fullerene polyhedron into a string of pentagons and hexagons, and the locations of the pentagons in that sequence result in the 12 ring- (or face-) spiral pentagon indices (RSPI) that uniquely determine the fullerene graph \( G_F \) up to isomorphism. The RSPI is thus a compact, unique, and canonical representation of fullerene isomers, from which their graphs can easily be constructed. The success of the MF face-spiral algorithm made it tempting to conclude that every fullerene can be constructed in this manner because it holds true for the first many million isomers.1,2 However, this is not so. Manolopoulos and Fowler found the first counterexample in 1993, showing the existence of a \( T-C_{380} \) fullerene isomer that cannot be constructed from a face spiral.3 We call such fullerenes nonface-spiral or simply nonspiral (NS) fullerenes in the following. It appears that nonspiral fullerenes are exceedingly rare. The first two nonspiral fullerenes are \( T-C_{380} \) and \( D_3-C_{384} \), which are shown in Figures 1 and 2. In fact, Brinkmann et al. demonstrated that these are the only two NS-fullerenes out of 2,653,602,561,199 fullerenes with 400 atoms or less.6-8

Figure 1. Density functional (B3LYP) optimized structure of the NS-fullerene \( T-C_{380} \). View from the top (left) and side (right) of the polyhedron.

Hence, it is advantageous to identify fullerenes with their canonical face spiral and to treat the very rare fullerenes that do not have one separately.

We recently introduced a comprehensive software package called Fullerene, which is a general purpose program for automatically constructing, transforming, and analyzing fullerenes.9 The program allows constructing any fullerene (whether or not it has a face spiral) from generalized ring spiral indices by way of a new algorithm and analyzing

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topological as well as chemical properties. It produces good approximations to the molecular structures by way of force-field optimization, resulting in geometries that are close to those calculated by a much more demanding quantum theoretical treatment.

The aim of this study was to investigate the structure and topology of the smallest three NS-fullerenes, T-C_{380}, D_{15}-C_{384}, and D_{15}-C_{440}, as well as the smallest known NS-fullerene with no adjacent pentagons, D_{15}-C_{672}, using density functional theory (DFT) in order to obtain accurate structural properties. We further aim to study the leapfrog and halma transforms of T-C_{380}, D_{15}-C_{384}, D_{15}-C_{440}, and D_{15}-C_{672}, which are special cases of Goldberg–Coxeter transformations,¹⁰,¹¹ to highlight some important mathematical properties for this class of NS-fullerenes.

**Methods.** Our program, Fullerene,⁹ first creates the fullerene graph G_f for each fullerene considered, applying the algorithms as discussed in the next section. The fullerene graph is an undirected, planar, cubic, and connected graph describing the C–C bonds, which uniquely determines a particular fullerene up to inversion. Pairs of enantiomers share the same underlying graph. All four investigated fullerenes as well as the derived structures are chiral, but as electronic and geometric properties are independent of inversion, we do not distinguish between the enantiomers. To generate the three-dimensional molecular structure, the program uses the Tutte embedding algorithm¹² to compute a planar layout of G_f, which is then projected onto a sphere to produce a 3D surface structure without crossing edges. This initial structure is then subjected to a force-field optimization specifically designed for fullerenes as described in detail in ref 9.

The force-field optimized structures were taken as input for a refined density functional theory (DFT) optimization, using the gradient corrected Perdew–Burke–Ernzerhof (PBE)¹³ functional and the hybrid Becke–Lee–Yang–Parr (B3LYP)¹⁴,¹⁵ functional together with a def2-SVP basis set¹⁶ and the resolution of identity (RI) approximation.¹⁷ Energies and gradients were obtained with the Turbomole and Gaussian09 program packages.¹⁸,¹⁹ Convergence criteria were tightened with respect to the standard values (SCF convergence <10⁻¹⁰ a.u., root-mean-square force <10⁻³ a.u., and fine grid for the numerical integration). The optimized structures of T-C_{380} and D_{15}-C_{384} are shown in Figures 1 and 2. The next NS-fullerene, D_{15}-C_{440}, which is similar in shape compared to D_{15}-C_{384}, is shown in Figure 3. The first NS-fullerene with isolated pentagons is D_{15}-C_{672} and is shown in Figure 4. We note that the force-field implemented in Fullerene gives very good initial structures, e.g., the root-mean-square error in the force-field optimized bond distances is ≈0.12 Å compared to the PBE optimized structure.

For each of the four NS-fullerenes, we performed Goldberg–Coxeter (GC) transformations²⁰,²¹ T_{k,l}(G_f) for the special cases k = l, and for l = 0, in order to investigate whether or not these fullerenes can be unwound into a face spiral. We considered GC-transformed fullerenes up to k = 7 for l = 0, and to k = 4 for k = l. These very large structures, comprised of thousands of atoms, were not subjected to DFT optimizations because of the excessive computer time required but only to force-field optimizations.

In addition, we carried out B3LYP optimizations for the most stable isomer for a series of C_{3n} structures in the range 20 ≤ N ≤ 540 to compare to the stability of the NS-fullerenes. Here, we used an augmented correlation consistent PVDZ basis set for 20 ≤ N ≤ 60, a correlation consistent PVDZ basis set for 60 ≤ N ≤ 180, and a 6-31G basis set²⁹ for the larger fullerenes with 240 ≤ N ≤ 540.

### RESULTS AND DISCUSSION

**Construction of T-C_{380} from T-C_{364} and D_{15}-C_{384} from D_{15}-C_{366} through Vertex Insertions.** The concept of vertex insertions or deletions and formal isomerizations has proven to be useful, as it allows for the stepwise derivation of one fullerene graph from another.²⁰,²¹ In particular, fullerene graphs that fail to be constructed using the MF face-spiral algorithm can be derived from smaller fullerenes that admit a spiral by vertex insertions.

Any patch of hexagons and pentagons can be characterized by its boundary code.²¹,²² Any two such patches that are equal in their boundary code can be exchanged for each other. Furthermore, if the symmetry of the boundary code is higher than the symmetry of the patch itself, the patch can be replaced by a rotated instance of itself. The smallest example of such a...
Rotation is the Stone–Wales transformation. Two patches with the same boundary code must have the same number of pentagons in order to keep the number of pentagons exactly at 12 in the overall fullerene graph, as required by Euler’s...
polyhedron formula. They can, however, differ in their number of hexagons. In patches that contain at most one pentagon, the number of hexagons is uniquely defined by their boundary, i.e., vertex insertions can only be performed by replacing patches that contain at least two pentagons. Two hexagon-only patches with the same boundary are, however, only guaranteed to be isomorphic if they consist of no more than 24 vertices.

In the case of a constant number of hexagons, a patch replacement is formally an isomerization. Notable examples are the Stone–Wales transformation and the generalized Stone–Wales transformation. Formal isomerizations can be represented as the application of two-switches to a limited domain of the graph. According to Berge’s switching theorem, every fullerene graph of a given size can be derived from one isomer of the same size by consecutive two-switches.

In the case of a differing hexagon count, the transformation is called a formal vertex insertion or deletion. The first described examples are the Endo–Kroto two-vertex insertion, Yoshida–Fowler four-vertex insertion, and Yoshida–Fowler six-vertex insertion. Brinkmann et al. compiled extensive lists of formal isomerizations and formal vertex insertions.

According to Hasheminezhad et al., every fullerene can be derived from either $C_{20}$ or $T_2C_{28}$ by applying a sequence of vertex insertions. These vertex insertions (also referred to as “growth operations”) are divided into three classes, two of which are of countably infinite size. Hence, every fullerene can be constructed from $C_{20}$ or $T_2C_{28}$ (which both admit a spiral), every nonspiralable fullerene can be derived from spiralable fullerenes by applying one or several vertex insertions.

More concretely, the substitution of one patch of vertices for another containing less vertices can be understood as the truncation of a domain of high curvature in the corresponding polyhedron. The curvature (which must always sum to $4\pi = 12\pi/3$ in total) is thereby spread, and the distance between some or all pentagons involved increases. Vice versa, the addition of vertices resembles the capping of one or several faces. As a result, the distance between pentagons in the replaced patch decreases. It is not possible to truncate or cap a domain that contains one or no pentagon. The property of not having a face spiral is a global property of a fullerene graph and cannot be related to a specific subgraph. However, failing spirals typically fail at domains of high curvature, i.e., a subgraph that contains many pentagons in close proximity.

The NS-fullerenes $T_C380$ and $D_C384$ can be constructed by subsequent Yoshida–Fowler four-vertex (YF4) insertions and Brinkmann–Fowler six-vertex (BF6) (denoted as G4.14.4.1 $\leftrightarrow$ G4.14.2.2 by Brinkmann et al.) insertions, respectively, as shown in eq 1.

$$
T_C380 \leftrightarrow YF4 \leftrightarrow C_3-C_384 \leftrightarrow BF6 \leftrightarrow D_C384
$$

The DFT optimized structures of $T_C364$ and $D_C384$ from which $T_C380$ and $D_C384$ are constructed, are shown in Figure 5. The corresponding face-spiral pentagon indices are listed in Table 1. $T_C364$ has no pentagon start for a face spiral, whereas $D_C366$ does. From Table 2, we also see that $D_C366$ admits more face spirals compared to $T_C364$. All fullerenes leading to $D_C384$ by Brinkmann–Fowler six-vertex insertions have face spirals starting at a pentagon, while the ones leading to $T_C380$ by Yoshida–Fowler four-vertex insertions have no pentagon start.

### Table 1. Goldberg–Coxeter Indices ($k$, l), Triangulation Parameter $t(k,l)$, Number of Vertices $n_v$, Number of Symmetry-Distinct ($NS^D$) and Total ($N_s$) Face Spirals, Pentagon Neighboring Index $N_p$, Hexagon Strain Parameter $\sigma_h$, HOMO–LUMO Gap $\Delta_{\text{HLL}}$, from a Hückel Analysis (in eV), Wiener Index $W$, and Szeged Index $S_z$ of the Halma and Leapfrog Transforms of $C_{364}$ and $C_{366}$

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<th>$NS^D$</th>
<th>$N_s$</th>
<th>$N_p$</th>
<th>$\sigma_h$</th>
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More concretely, the substitution of one patch of vertices for another containing less vertices can be understood as the truncation of a domain of high curvature in the corresponding polyhedron. The curvature (which must always sum to $4\pi = 12\pi/3$ in total) is thereby spread, and the distance between some or all pentagons involved increases. Vice versa, the addition of vertices resembles the capping of one or several faces. As a result, the distance between pentagons in the replaced patch decreases. It is not possible to truncate or cap a domain that contains one or no pentagon. The property of not having a face spiral is a global property of a fullerene graph and cannot be related to a specific subgraph. However, failing spirals typically fail at domains of high curvature, i.e., a subgraph that contains many pentagons in close proximity.

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Construction of NS-Fullerenes through a Generalized Face Spiral. NS-fullerenes can only practically be found through an extensive search through all possible isomers by using efficient algorithms such as the Brinkmann–Goedgebeur–McKay patch replacement algorithm. Once an NS-fullerene has been found, it can be completely characterized by a generalized face-spiral algorithm, which we will describe in this section.

The MF face-spiral algorithm was the first algorithm for creating fullerene graphs of a given size. Furthermore, it offers a short and unambiguous description of fullerene graphs. It works as follows. In the dual of the cubic graph (which is a triangulation of the sphere), three vertices that are mutually connected, i.e., form a face, are chosen as a starting sequence. The remaining vertices are then added one-by-one, such that the next vertex is connected to the previous one and to the vertex that has been added earliest and which has open valencies left. By this procedure, a spiral that contains all vertices of the triangulation—is obtained. In other words, a face spiral in a fullerene is identical to a Hamiltonian spiral path for the fullerene dual. Giving the degree of the vertices (5 or 6 in the case of fullerene graphs) in the order in which they are added allows for adding a vertex to the spiral without disconnecting the remaining subgraph is chosen. By demanding that the remaining subgraph must always remain connected, we ensure that the spiral never gets stuck, and hence, every fullerene graph can be constructed and described with a general spiral string. As we prove in a forthcoming paper, this algorithm is guaranteed to work for all connected planar cubic graphs.

The general pentagon indices are denoted as $n_1,k_1,...,n_m,k_m,p_1,...,p_{12}$. Where $n_i,k_i$ are the positions at which a jump is performed and the respective offset, and $p_i$ are the positions of the 12 pentagons. Counting jump- and pentagon-positions starts from 1. If the jump list is empty, we omit the semicolon. The general spiral code describing the spiral in Figure 7(b) is “14,1,12,3,5,8,9,11,12,13,14,15,16”, where $n_1,k_1 = 14,1$ indicates that a cyclic shift of length 1 is performed before adding face 14.

We define the canonical general spiral of a graph as the shortest of the 6$n_i$ spiral codes (where $n_i$ is the number of vertices in the cubic graph). If there is more than one shortest spiral code, the lexicographically smallest is chosen. Equations 2–5 list the canonical general spiral codes of the fullerene graphs that are investigated in this paper.

$$C_{150^3}: 110, 2 \rightarrow 45, 70, 71, 82, 83, 110, 119, 120, 144, 184, 185, 192$$

$$C_{144^3}: 49, 1 \rightarrow 29, 30, 31, 49, 145, 146, 170, 171, 190, 191, 192, 194$$

$$C_{142^3}: 62, 1 \rightarrow 39, 40, 41, 62, 170, 171, 197, 198, 218, 219, 220, 222$$

$$C_{142^3}: 100, 1 \rightarrow 142, 1 \rightarrow 51, 53, 109, 111, 220, 252, 288, 302, 304, 306, 320, 338$$

Figure 6. Two attempts to construct a spiral in the $D_3$ isomer of C$_{28}$: (a) succeeds while (b) misses face 16.
Electronic Structure, Stability, and Geometry of NS-Fullerenes. The smallest NS-fullerene $T-C_{380}$ has a large HOMO–LUMO gap of $\Delta E_{HL} = 0.434$ eV obtained from a Hückel analysis (Table 3). This compares well with the DFT calculations, which give $0.289$ eV at the PBE and $0.640$ eV at the B3LYP level of theory (the larger gap for the latter functional comes from the exact exchange contribution). $D_{3}$- $C_{440}$ has a HOMO–LUMO gap of $0.055$ eV, as shown in Table 4. In contrast, $D_{3}$-$C_{384}$ and $D_{3}$-$C_{672}$ have a zero gap and should undergo a first-order Jahn–Teller distortion into $C_{3}$ symmetry (active E-mode). Structurally, these Jahn–Teller distortions are extremely small for such large fullerenes and not visible to the naked eye. For example, for $D_{3}$-$C_{384}$ the optimized distances around the three bonds sharing two pentagons where the $C_{2}$ axes are situated are $1.4567$, $1.4567$, and $1.4570$ Å (at the optimized B3LYP level of theory). In $D_{3}$-symmetry, these distances are all equal. However, the DFT calculations show an increased HOMO–LUMO gap of $0.291$ eV for $D_{3}$-$C_{384}$ using the PBE functional as compared to simple Hückel theory.

Concerning the stability of these fullerenes, we can compare to $C_{60}$ by using the following (hypothetical) reaction, which approximates the energy difference per atom

$$\frac{1}{60} C_{60} \rightarrow \frac{1}{N} C_{N} + \Delta E_N$$

The results together with some other useful information of the optimized DFT structures are shown in Table 5. Figure 8 shows the stability of the four NS-fullerenes compared to a selection of the most stable fullerenes within a series of isomers from $C_{20}$ to $C_{540}$. Here $\Delta E_N$ is plotted against $N^{-1/2}$ in order to extrapolate to the graphene limit ($N \rightarrow \infty$). We note in passing that in cluster physics a $N^{-1/3}$ behavior is chosen for compact 3D clusters to extrapolate to the solid state. This well-known behavior is derived for example from a liquid-drop model expansion of the free energy.36,37 For fullerenes, the atoms are on the surface of a “sphere”, which more realistically points toward a $N^{-1/2}$ behavior. Indeed, this law gives a much better correlation with the calculated $\Delta E_N$ values and is therefore applied here.

We first see that the fullerenes separate into two distinct sets, $C_{N<60}$ and $C_{N>60}$ for the most stable fullerenes, the latter fulfilling the isolated pentagon rule (IPR). This results in two stability lines. Second, for the most stable IPR fullerenes, one obtains the graphene limit at $-13$ kcal/mol, in reasonable agreement with the estimated value of $-9$ kcal/mol obtained from heat of formation of graphite and considering the van der Waals interaction between graphene layers.36,37 Third, the results show that the NS-fullerenes are reasonably stable with a destabilization of less than $2$ kcal/mol per C–C bond compared to the most stable IPR fullerenes. The PBE and B3LYP results are very similar.

Table 5 contains many other useful properties. We see that $T-C_{364}$ and its Yoshida–Fowler vertex inserted $T-C_{380}$ have very similar volumes and surface areas (trivially the surface area increases from $T-C_{364}$ to $T-C_{380}$) and so do $D_{3}$-$C_{366}$ and $D_{3}$-$C_{384}$. However, a fullerene with a larger number of vertices does not have to be larger in size due to their completely different geometry, as shown by a comparison, for example, between $T-C_{364}$ and $D_{3}$-$C_{384}$. Except for $C_{60}$ all fullerenes listed in Table 5 are slightly nonconvex, as shown by the (surface) convexity parameter $C_r = A_{CH}/A$. Here, $A$ is the surface area of the fullerene, and $A_{CH}$ the surface area of its convex hull. The nonconvexity of the fullerenes is clearly visible in Figures 1–5, where we see a slight concave curvature around the hexagons.

The last three columns in table 5 measure the deviance for each fullerene from the ideal 3D sphere (for a detailed discussion see ref 9).

Table 3. Goldberg–Coxeter indices $(k,l)$, Triangulation Parameter $t(k,l)$, Number of Vertices $n_{s}$, Number of Symmetry-Distinct (N$_{SD}^{(k)}$) and Total (N$_{t}$) Face Spirals, Pentagon Neighboring Index N$_{p}$, Hexagon Strain Parameter $\sigma_{H}$, HOMO–LUMO Gap $\Delta E_{HL}$ from a Hückel Analysis (in eV), Wiener Index $W$, and Szeged Index $S_{s}$ of the Halma and Leapfrog Transforms of C$_{380}$

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Table 5. Properties Obtained from DFT Optimizations

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<th>fullerenes</th>
<th>DFT</th>
<th>( \tau_{\text{min}} )</th>
<th>( \tau_{\text{max}} )</th>
<th>( \tau_{\text{MCS}} )</th>
<th>( \Delta \varepsilon_{\text{HOMO-LUMO}} )</th>
<th>( V )</th>
<th>( A )</th>
<th>( C_A )</th>
<th>( \phi_{\text{DPE}} )</th>
<th>( D_{\text{MDES}} )</th>
<th>( \lambda_{\text{asym}} )</th>
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<tr>
<td>( I_7^C_{384} )</td>
<td>PBE</td>
<td>1.407</td>
<td>1.457</td>
<td>3.565</td>
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<td>164.8</td>
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<td>0.758</td>
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<td>40.7</td>
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<td>0.567</td>
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<td>0.697</td>
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<td>1.067</td>
<td>0.513</td>
<td>47.4</td>
<td>39.63</td>
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<tr>
<td>( D_7^C_{672} )</td>
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\( \Delta \varepsilon_{\text{HOMO-LUMO}} \) is the energetic stability in kcal/mol per carbon atom compared to \( \varepsilon_{\text{HOMO}} \) in kcal/mol as defined in eq 6. Volume \( V \) in \( \text{Å}^3 \) and surface area \( A \) in \( \text{Å}^2 \), convexity parameter \( C_A \), isoperimetric quotient \( \phi_{\text{DPE}} \), spherical distortion parameter from minimum distance sphere \( D_{\text{MDES}} \) in \%, and Fowler asymmetry parameter \( \lambda_{\text{asym}} \).
HALMA AND LEAPFROG TRANSFORMS OF NS-FULLERENES

The Goldberg–Coxeter transformation,\textsuperscript{10,11} \(T_{k,l}^{\text{GC}}\), transforms a fullerene with vertex number \(n_v = N\) to a larger fullerene with \(n_v = N(k^2 + kl + l^2)\), where \(k\) and \(l\) are integers. Two particularly simple GC transforms are the halma and leapfrog transformations, corresponding to \(l = 0\) and \(k = l\), respectively. We call the \(l = 0\) case, which is shown in Figure 9(a), the “halma” transform due to the construction’s similarity to a halma game board. It is also sometimes called a \(k\)-inflation. The leapfrog transformation is illustrated in Figure 9(b).

We briefly mention some important properties of GC transformations. The GC transform can be described in terms of multiplication by complex numbers \((k + l\omega)\), where \(\omega = e^{2\pi i/6}\), in what is called the Eisenstein plane.\textsuperscript{2}

Because of this, any number of GC transformations can be composed into a single GC transformation, corresponding to the product of the Eisenstein numbers, as follows:

\[
T_{k,l}^{\text{GC}} = T_{k,0}^{\text{GC}} T_{0,k}^{\text{GC}}
\]

The GC transform is 12-fold symmetric through the transformations:

\[
\omega^j \rightarrow \omega^{j+6}\text{ for } 0, ..., 5
\]

From eq 7, we can derive the combined leapfrog and halma transformations:

\[
T_{1,0}^{\text{GC}} = T_{1,0}^{\text{GC}} T_{0,1}^{\text{GC}}
\]

\[
T_{k,0}^{\text{GC}} T_{0,k}^{\text{GC}} = T_{k,k}^{\text{GC}}
\]

Hence, we obtain all possible GC transformations of the form \(T_{1,0}^{\text{GC}}\) and \(T_{0,1}^{\text{GC}}\) from such combinations as implemented in Fullerene. The two largest halma transforms of C\textsubscript{380} and C\textsubscript{384} studied here are shown in Figures 10 and 11.

We can now state our main result:

**Conjecture.** Any halma transform of an NS-fullerene is also an NS-fullerene. If this conjecture is true, the class of NS-fullerenes is finite, even though it is vanishingly small compared to the class of all fullerences for the range where exhaustive search has been performed, and we expect it to be so for larger \(N\) as well.

In Tables 3 and 4, we see that many of the leapfrogged NS-fullerenes are NS-fullerenes themselves but that in general they are not. Brinkmann and Fowler have investigated spiralability of the leapfrogs of several million cubic polyhedra and found that these leapfrogs statistically are less likely to have spirals than their parents.
We see from Table 5 that a leapfrog of a spiralable fullerene can be either spiralable or nonspiralable. For example, \( T_{1,1}^{GC}[C_{440}] \) admits a spiral, but \( T_{1,1}^{GC}[C_{440}] = T_{1,0}^{GC}[C_{440}] \) does not. Similarly, the halma transform of a spiralable fullerene can be either; NS-D_3-C_672 provides a counterexample to the spiralable fullerenes being closed under the halma transform because it can be written as the halma transform \( T_{1,0}^{GC}[D_3-C_{368}] \).

The face-spiral pentagon indices for \( D_3-C_{168} \) are given in Table 1. As expected, the spiral count for the \( D_3-C_{368} \) fullerene is low, i.e., we get 11 distinct face spirals out of a total of only 66. NS-D_3-C_672 is likely to be the smallest Goldberg–Coxeter fullerene. We mention that the \( D_3-C_{384} \) may well be the first leapfrog NS-fullerene.

For completion and future reference, we also list topological indicators (Wiener and Szeged index) for C_{364}, C_{366}, C_{380}, C_{384}, C_{440}, and C_{672} and their smallest Goldberg–Coxeter transforms for \( l = 0 \) or \( l = k \) in Tables 2, 4, and 5.

**CONCLUSIONS**

We investigated the four NS-fullerenes, NS-T-C_{380}, NS-D_3-C_{380}, NS-D_3-C_{440}, and NS-D_3-C_{672}, as well as their leapfrog and halma transforms up to about 30,000 atoms. The NS-fullerenes were optimized and analyzed quantum chemically at the DFT level of theory, while the larger transformed fullerenes were force-field optimized and analyzed using graph theoretical methods.

NS-T-C_{380} has a large HOMO–LUMO gap of 0.434 eV, while C_{440}, C_{380}, and C_{672} have a small or zero gap, which places them among the semiconductors and conductors, respectively.

The predicted Jahn–Teller distortion undergone by the zero gap fullerenes was found to be so minor as to be undetectable by visual inspection of the structure.

NS-fullerenes typically have clusters of pentagons in close proximity, leading to sharp curvature and reduced stability compared to more spherical fullerenes of equal size, but the investigated NS-fullerenes remain reasonably stable with less than 2 kcal/mol difference per bond to the icosahedral isomers. All four quantum chemically optimized geometries are found to be slightly concave, a feature that is predicted by the force-field optimization, showing that the concavity arises directly from the graph topology rather than the electronic structure.

It was found that the leapfrog transformation may introduce spirability, while all the halma-transformed fullerenes were unspiralable. We conjecture that this class of NS-fullerenes is closed under the halma transform. However, the converse is not true; a counterexample is NS-C_{672}, which is the second halma transform of C_{168}.

While the vanishingly small proportion of isomers with no spirals makes it difficult to find examples of NS-fullerenes through extensive search, especially for large values of \( N \), new NS-fullerenes can be obtained from existing ones through halma transformations if our proposed conjecture holds. Furthermore, we conclude that none of the investigated leapfrogs of NS-T-C_{380} are spiralable.

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**Notes**

The authors declare no competing financial interest.

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