Fullerenes 5

Mircea V. Diudea

Faculty of Chemistry and Chemical Engineering
Babes-Bolyai University
400028 Cluj, ROMANIA
diudea@chem.ubbcluj.ro
Contents

- Fullerene - Physico-Chemical properties
- Addition Reaction
- Stone-Wales Reactions
Fullerenes in Nature

- Fullerenes were found in the natural environment, but only in the ppm-range. Some places are Shunga/Russia,¹ New Zealand² and Sudbury/Canada.³

Isolated Fullerenes

$C_{60}$  $C_{70}$
Fullerenes - physico-chemical properties

- Good solvents for fullerenes are CS₂, toluene, xylene, and o-dichlorobenzene while they are insoluble in water and stable at air.
- Thin layers of fullerenes and solutions are coloured, because of ππ*-electron transitions:¹
  - C₅₆ purple/violet
  - C₇₀ brick-red
  - C₇₆ light yellow-green
  - C₂ᵥ⁻C₇₈ maroon, D₃⁻C₇₈ golden,
  - C₄₄ brown and
  - C₈₅ olive-green.

Chemical Reactions of Fullerenes

- Fullerenes are not “aromatic” compounds.¹
- No reactions with “reversion to type” (preserving e.g., the π-electron distribution, as the substitution reactions of benzene - like molecules, i.e., aromatic species) occur.
- The general addition chemistry of C₆₀ is closer to “super alkenic” than “super aromatic”.²

Addition Reactions

- Fullerenes are electron-deficient molecules.¹
- They form multiple-charged anions with electron donating species, *e.g.*, the alkaline or alkaline-earth metals.
- **Endohedral complexes**, like La@C₈₂, are formed when the metal was catalysed the fullerene growth.
- **Exohedral derivatives** are synthesized by addition reactions.

Endohedral (a) and exohedral (b) derivatives

(a) La@C$_{82}$

(b) C$_{60}$Cl$_6$
Addition Reactions

- Although $C_{60}$ has 12500 Kekule structures,¹ its addition reactions, in which it shows an electron-deficient alkenic character, are oriented by the Fries Kekule structure;
- recall that, in this unique structure, all $p$ (5,6) edges are formal single bonds while all $h$ (6,6) are formally double.
- The highest bond order (i.e., the 2-order) is reached by the Stone-Wales formal double bonds, located at the centre of pyracylene-like patches.
- All 30 double bonds of $C_{60}$ (among 90 edges) while in $C_{70}$ (among 105 edges) only 20 are of this type. The addition reaction will occur, most probably, at these electron-rich bonds.

Stone-Wales isomerisation

The bold edge shares two cycles of size \((s_m, s_n)\) to be reduced, after rotation, to \((s_{m+1}, s_{n+1})\).

The two cycles joined by this edge will increase their size from \((s_{p}, s_{r})\) to \((s_{p+1}, s_{r+1})\).

**Stone-Wales isomerisation**

Most often, the edge flipping runs as a *cascade SW* transformation.

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Stone-Wales isomerisation

- **SW Isomerization** by a concerted mechanism, with a diradical transition state.
**Stone-Wales isomerisation**

- **SW** Isomerization involving a carbene as the intermediate.
Enantiomers by SW: $C_{28}:1$
A SW Family - $C_{30}$

$C_{30} : 1$

$C_{30} : 2$

$C_{30} : 3$
Coalescence of Nanostructures

SW edges

M. V. Diudea, Cs. L. Nagy, O. Ursu, and T. S. Balaban,
ta-Tubulenes
fa - Tubulenes

fa - Tubulenes from ta - Tubulenes by SW isomerization

\[ C_{96}(6^6(5,6)^6(6,6)^6(6,5)^66^6) (D_{6d}) \]

Geodesic Projection

kfz-peanut Tubulenes
**Peanut**$^1$ $kf$-Tubulenes $C_{NN'}(k\in\mathbb{Z}[2k,n])$

<table>
<thead>
<tr>
<th>$C_{168}(6\ 6\ (5,6)\ (6,5)\ 7\ 6\ 6\ 6\ 7\ )$</th>
<th>$C_{168}(6\ 6\ (5,6)\ (6,5)\ 7\ (5,7)\ 3\ (7,5)\ 3\ 6\ )$</th>
</tr>
</thead>
</table>

Peanut $k_f$-Tubulenes

Isomerization of the distancing nanotube by SW edge rotations

$C_{72}(7^6 6^6 6^6 7^6)$

Geodesic projection

Peanut *kf*-Tubulenes

Isomerization of the distancing nanotube by SW edge rotations

C$_{72}(^6 5 6^4 7 7 6^4 5 7^6)$

Geodesic projection

Peanut \textit{kf}-Tubulenes

Isomerization of the distancing nanotube by SW edge rotations

\begin{align*}
C_{72}(7^6 5^2 7^2 6^2 5 7 5 7^5)
\end{align*}

Geodesic projection

Peanut $k_f$-Tubululenes

Isomerization of the distancing nanotube by SW edge rotations

$C_{72}(7^6 5^2 7^5 7^2 6^2 5^7 5 7^6)$

Geodesic projection

Energetic and Spectral Properties of Peanut $kfz$-Tubulenes $C_N(k..Z[2k,n])$

<table>
<thead>
<tr>
<th>Cage</th>
<th>Sym</th>
<th>PM3 HF/at</th>
<th>PM3 Gap</th>
<th>Spectral Data</th>
<th>Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 $C_{168}(6^6 5^6 6^6 7^6 7^6 6^6 6^6 6^6)$</td>
<td>$D_{6d}$</td>
<td>11.927</td>
<td><strong>5.11</strong></td>
<td>$-0.023$</td>
<td>-0.023</td>
</tr>
<tr>
<td>4 $C_{168}(6^6 5^6 6^6 7^6 7^6 6^6 6^6 7^6)$</td>
<td>$C_2$</td>
<td>12.261</td>
<td><strong>5.16</strong></td>
<td>$-0.013$</td>
<td>-0.023</td>
</tr>
<tr>
<td>5 $C_{168}(6^6 5^6 6^6 7^6 7^6 6^6 7^6 6^6 6^6 7^6)$</td>
<td>$C'_3$</td>
<td>12.452</td>
<td><strong>5.19</strong></td>
<td>0.009</td>
<td>-0.040</td>
</tr>
<tr>
<td>6 $C_{168}(6^6 5^6 6^6 7^6 7^6 6^6 7^6 6^6 7^6 6^6 7^6)$</td>
<td>$S'_6$</td>
<td>12.553</td>
<td><strong>5.43</strong></td>
<td>0.162</td>
<td>-0.040</td>
</tr>
</tbody>
</table>
Tubulene (left) and peanut $z$-tubulenes (mean) corresponding to the multi-peanut $(C_{60})_n$ (right)
HOMO eigenvalues of multi peanut z-tubulenes \((C_{60})_4\)
((5,7)3) kz-peanut
Tubulenes
Rearrangement of (4, 6) pairs to (5, 5) ones by SW edge rotation

$C_{84}(7^7 5^7 (4,6)^7 7^7 5^7)$

$C_{84}(7^7 5^7 14^7 7^7); (C_i)$

Rearrangement of all (5, 7) cages to the classical $C_{12k}$ fullerenes by SW$^1$

$C_{60}(5^{5}75^{10}5^{5}) (C_{i})$

$C_{60}(5^{5}(5,6)^{5}(6,5)^{5}5^{5}) (/_{h})$

# Semiempirical and spectral data for ((5,7)3) periodic cages

<table>
<thead>
<tr>
<th>(5,7) Cage</th>
<th>Sym</th>
<th>PM3 HF/lat</th>
<th>PM3 GAP</th>
<th>Spectral Data</th>
<th>Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{N}(k^5, 7, 5, 7, 5, 2k))</td>
<td></td>
<td>(\Lambda_{N/2})</td>
<td>(\Lambda_{N/2+1})</td>
<td>GAP</td>
<td>Shell</td>
</tr>
<tr>
<td>1</td>
<td>60; 5; 1</td>
<td>(C_i)</td>
<td>21.158</td>
<td>5.623</td>
<td>0.3797</td>
</tr>
<tr>
<td>2</td>
<td>100; 5; 2</td>
<td>(C_i)</td>
<td>18.906</td>
<td>5.592</td>
<td>0.2785</td>
</tr>
<tr>
<td>3</td>
<td>140; 5; 3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2979</td>
</tr>
<tr>
<td>4</td>
<td>84; 7; 1</td>
<td>(C_i)</td>
<td>16.249</td>
<td>4.538</td>
<td>0.2452</td>
</tr>
<tr>
<td>5</td>
<td>140; 7; 2</td>
<td>(C_i)</td>
<td>15.828</td>
<td>5.114</td>
<td>0.2231</td>
</tr>
<tr>
<td>6</td>
<td>196; 7; 3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2199</td>
</tr>
</tbody>
</table>
((5,7)3) Periodic Cages

- The ((5,7)3) periodic cages tend to isomerize to the more stable \(fa\)-tubulenes
ISOMERIZATION OF (5, 7) PERIODIC CAGES

to fa-Tubulenes

\[ C_{100}(k^5 (7^5 7^5) 5^k k^r k); \ k = 5; \ r = 2 \]

\[ C_{100}(5^5 6^5 (5,6)^5 -A[10,2]) \]
ISOMERIZATION OF (5, 7) PERIODIC CAGES

\[ C_{100}(k^{5}k^{7}5^{8}(5,6)(5,7)5^{k}k); \]
\[ k = 5 \]

\[ C_{100}(k^{5}k^{7}(5,6)(6,6)(6,5)7^{k}5^{k}k); \]
\[ k = 5 \]
ISOMERIZATION OF (5, 7) PERIODIC CAGES

\[ C_{100}(k_6^{k_6}, k_5^{k_5}, k_7^{k_7}, k_5^{k_5}, k_5^{k_5}, k_6^{k_6}) \]

\[ k = 5 \]
Data for some ((5,7)3) peanut cages and their isomerization to *fa*-tubulenes

<table>
<thead>
<tr>
<th>Cage</th>
<th>Sym</th>
<th>PM3 HF/at</th>
<th>PM3 GAP</th>
<th>Spectral Data GAP</th>
<th>Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $C_{100}(k^5, 7^5, k_r, k^5)$; $k = 5; r = 2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 $C_{100}(k^6, (5,6)^5, (5,7)^7, (5,6)^k, (5,6)^k)$</td>
<td>$D_{5d}$</td>
<td>15.146</td>
<td>5.546</td>
<td>0.311</td>
<td>0.311</td>
</tr>
<tr>
<td>3 $C_{100}(k^6, (5,6)^5, (5,8)^5, (5,6)^k, (5,6)^k, (5,6)^k)$</td>
<td>$C_{5v}$</td>
<td>13.966</td>
<td>5.770</td>
<td>0.391</td>
<td>0.020</td>
</tr>
<tr>
<td>4 $C_{100}(k^5, 7^5, k_r, k^5, (5,6)^8, (5,7)^k, (5,6)^k)$</td>
<td>$C_1$</td>
<td>18.260</td>
<td>5.404</td>
<td>0.414</td>
<td>0.147</td>
</tr>
<tr>
<td>5 $C_{100}(k^5, k_r, k^5, (5,6)^5, (6,6)^7, (6,6)^k)$</td>
<td>$D_{5d}$</td>
<td>15.205</td>
<td>3.849</td>
<td>0.247</td>
<td>0.239</td>
</tr>
<tr>
<td>6 $C_{100}(5^6, 5^5, (5,6)^{-A(10,2)})$</td>
<td>$D_{5d}$</td>
<td>10.876</td>
<td>5.045</td>
<td>0.350</td>
<td>0</td>
</tr>
</tbody>
</table>
Functionalization of fullerenes
The study of 1,3-bipolar nitrilimines and fullerene C₆₀ cycloaddition

- During the study of 1,3-disubstituted nitrilimines and fullerene cycloaddition reaction a model set of fullerene pyrazolines containing various substituents including heterocyclic fragments and CF₃ group was synthesized. Stable [6,6]-closed adducts 1, 2, 3, 4, 5, 6, and 7 were synthesized by 1,3-bipolar cycloaddition of fullerene and nitrilimines, generated in situ from the corresponding hydrazonoil halogenides and threeethylamine.
Functionalization of fullerenes

Methanofullerenes

These compounds represent the most versatile and widely studied class of fullerene adducts. In theory, there exist four possible isomers: 6-5-open, 6-5-closed, 6-6-open, 6-6-closed, depending on whether addition takes place at 6-6 or 6-5 bonds and whether the bridgehead C atoms are at nonbonding distance or are connected by a transannular bond.
Formation of the parent 6-5-open (1) and 6-6-closed (2) methanofullerene (C$_{61}$H$_2$) isomers by 1,3-dipolar cycloaddition of diazomethane to C$_{60}$ to give a 6-6-fused pyrazoline intermediate followed by thermal or photochemical extrusion of N$_2$. 
Functionalization of fullerenes

6-6-fused pyrazoline intermediate
Functionalization of fullerenes

- 1,3-Dipolar cycloaddition of tertbutyl (t-Bu) diazoacetate yields a mixture of two diastereomeric 6-5-open (kinetic) and one 6-6-closed (thermodinamic) products.
The optically active fullerene-sugar conjugate 4 is obtained by the attack of a nucleophilic glycosylidene carbene (formed from the corresponding diazirine) to C$_{60}$.
Functionalization of fullerenes

In the Bingel reaction, \( \infty \)-bromo-malonates are deprotonated by a base and react as nucleophiles with \( C_{60} \) to give an intermediate anion, which, by displacement of the halide, closes the methano bridge to diesters such as 5.
Functionalization of fullerenes

Trimethylsilyl-protected 3-bromopenta-1,4-diyne reacts in the presence of bases with trimethylsilylethyne affords 7, which, upon electrolysis, yields a **conducting polymeric film** at the cathode (TMEDA, N,N,N,N',N'-tetramethylethylenediamine; Ph, phenyl; and Me, methyl).
Functionalization of fullerenes

Formation of methanofullerenes by nucleophilic addition of a phosphonium ylide, a Wittig reagent.
Functionalization of fullerenes

- A fullerene-dendrimer
Functionalization of fullerenes
Functionalization of fullerenes
Cyclopropanation Reactions

Trans-4-[60]fullerene bis-adducts – fluorescence studies

Dimeric $C_{60}$; a $[2 +2]$ cicloadduct

$C_{5-c2-2_7(\text{all sp2)}; 120; D_{5d}; \text{HF} = 10.625 \text{ kcal/mol}$

$C_{120} - (hh)$

$C_{120} - (\rho\rho-\sigma)$

S. Lebedkin, A. Gromov, S. Giesa, R. Gleiter, B. Renker
Cycloaddition \([2 + 3] = C_{120}O\)

Fullerenes - physical properties


- The chemistry of fullerenes also includes the synthesis of endohedral fullerenes having the formula $\text{M@C}_n$, where M stands for a metal atom inside the fullerene cage.

- These studies have suggested enormous potential and a wide range of applications for carbon-based materials, thanks to the possibility of tailoring their physical properties and performances.

- It was suggested that the superconducting critical temperature of doped fullerite increases with the curvature of fullerene cages, namely with the reduction of the cluster size from $\text{C}_{60}$ down to $\text{C}_{36}$, and perhaps $\text{C}_{28}$ and $\text{C}_{20}$.

- Moreover, an unexpected ferromagnetic behavior has been recently described in fullerenic materials.
Utilizations of Fullerenes

- Soft ferromagnetics,
- Organic conductors,
- Lubricant materials,
- Superconductivity, discovered in fullerene films doped with alkaline metals. The temperature of transition into this state, at 45 K is exceeded only by ceramic superconductors, but fullerene films have higher critical-current values.
- Applications in catalysis is also of interest.
References


References


