Study of the Si fullerene cage isomers

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Fullerenes

Definition:
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Closed-cage structures constructed by only pentagonal and hexagonal rings.
Fullerenes

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Closed-cage structures constructed by only pentagonal and hexagonal rings

(All the atoms are three-fold co-ordinated \(\Rightarrow sp^2\)-like bonding)
$C_{60}$ Buckminsterfullerene

...but not only $C_{60}$

How many pentagons and hexagons?

As a consequence of the Euler’s theorem for the geometrical solids, an N-atom fullerene has:
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- 12 pentagons
- \( \frac{N}{2} - 10 \) hexagons

\[ N = 20, 24, 26, \ldots, 2n, \quad n \in \mathbb{N} \]
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\[ N = 20, 24, 26, \ldots, 2n, \quad n \in \mathbb{N} \]

Different arrangement of the pentagons and the hexagons gives different structures (isomers)
How many isomers are they?

<table>
<thead>
<tr>
<th>N</th>
<th>Isomers</th>
<th>N</th>
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<th>N</th>
<th>Isomers</th>
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<tbody>
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<td>1</td>
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<td>271</td>
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<td>40</td>
<td>60</td>
<td>1812</td>
<td>80</td>
<td>31924</td>
</tr>
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</table>

What about Si fullerenes?

Bonding:

C : $sp^1, sp^2, sp^3$

Si : mainly $sp^3$ + dangling bonds
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General Conclusions for Si fullerenes:
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- Thermodynamically unstable structures (local minima of the PES)
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- They look like "puckered" balls (the Si atoms move radially inwards and outwards)
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However ...
Three-fold co-ordinated and/or fullerene-like Si systems

- Si surfaces
Three-fold co-ordinated and/or fullerene-like Si systems

- Si surfaces
- Si-C heterofullerenes and nanotubes
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- **Si surfaces**
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Consequently: Si fullerenes are of interest
To date studied Si fullerenes

• Not any systematic study of Si fullerenes and their isomers
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- Focused on highly symmetric starting structures (for example $I_h \text{Si}_{60}$)
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- Not any systematic study of Si fullerenes and their isomers
- Focused on highly symmetric starting structures (for example $I_h \text{ Si}_{60}$)
- Studied structures: $\text{Si}_N$, $N = 20 - 32, 36, 44, 50, 60, 70$
The system under consideration

$\text{Si}_{38}$

all the 17 isomers

and

$\text{Si}_{20}$

for comparison
The method for Global Optimization I

- **Molecular Dynamics At Constant Temperature**

\[ m \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i V - m\gamma \frac{E_K - E_T}{E_K} \frac{d\mathbf{r}_i}{dt} \]

\[ E_K = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 \quad E_T = \frac{f}{2} k_B T \]

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• Evolution of \( V = V(t) \) in time under constant temperature
The method for Global Optimization II

• Minima of $V(t)$ configurations: Initials for damping molecular dynamics
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• Damping Molecular Dynamics

$$m \frac{d^2 r_i}{dt^2} = -\nabla_i V \quad v_i(t + \delta t) = 0.99v_i(t)$$
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- Configuration of the global energy minimum
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- Configuration of the global energy minimum

In agreement with the Cambridge Cluster Database for the first 100 Lenard-Jones clusters

(http://www-wales.ch.cam.ac.uk/CCD.html)
### 38-atom fullerene isomers

Table A.3. Fullerene isomers of C\(_{38}\)

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Ring spiral</th>
<th>Point group</th>
<th>NMR pattern</th>
<th>Vibrations</th>
<th>Pentagon indices</th>
<th>Band gap</th>
<th>Transformations</th>
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<tbody>
<tr>
<td>38:1</td>
<td>1 2 3 4 5 7 15 17 18 19 20 21</td>
<td>(C_2)</td>
<td>19×2</td>
<td>108, 108, 108</td>
<td>0 2 6 2 0</td>
<td>0.0312</td>
<td>3(2)</td>
</tr>
<tr>
<td>38:2</td>
<td>1 2 3 4 5 9 13 17 18 19 20 21</td>
<td>(D_{3h})</td>
<td>1×2, 2×6, 2×12</td>
<td>28, 47, 19</td>
<td>0 0 6 0 6 0</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
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<td>1 2 3 4 5 12 13 15 17 19 20 21</td>
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<td>38×1</td>
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<td>1 2 3 4 5 13 14 15 17 18 19 21</td>
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<td>19×2</td>
<td>108, 108, 108</td>
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<td>0.2069</td>
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<td>38×1</td>
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</tr>
<tr>
<td>38:9</td>
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<td>(D_3)</td>
<td>1×2, 6×6</td>
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<tr>
<td>38:10</td>
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<td>(C_2)</td>
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<td>38:11</td>
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<tr>
<td>38:12</td>
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<td>(C_{2v})</td>
<td>5×2, 7×4</td>
<td>83, 108, 83</td>
<td>0 0 8 4 0 0</td>
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<tr>
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<td>1 2 3 5 10 11 13 15 16 17 19 20</td>
<td>(C_2)</td>
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<td>5(2), 8(2), 10(2), 13, 17(2)</td>
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<td>38:14</td>
<td>1 2 3 5 10 12 14 15 16 17 19 20</td>
<td>(C_1)</td>
<td>38×1</td>
<td>108, 108, 108</td>
<td>0 1 0 1 0 0</td>
<td>0.1036</td>
<td>8(2), 11, 15, 16, 17</td>
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<tr>
<td>38:15</td>
<td>1 2 3 5 11 12 14 15 16 17 18 20</td>
<td>(C_{2v})</td>
<td>7×2, 6×4</td>
<td>84, 108, 84</td>
<td>0 0 10 2 0 0</td>
<td>0.0311</td>
<td>14(4)</td>
</tr>
<tr>
<td>38:16</td>
<td>1 2 3 10 11 12 13 14 15 16 17 18</td>
<td>(C_{3v})</td>
<td>2×1, 4×3, 4×6</td>
<td>57, 57, 57</td>
<td>0 0 12 0 0 0</td>
<td>0.0454</td>
<td>14(6)</td>
</tr>
<tr>
<td>38:17</td>
<td>1 2 4 7 9 10 12 13 15 18 20 21</td>
<td>(C_2)</td>
<td>19×2</td>
<td>108, 108, 108</td>
<td>0 2 10 0 0 0</td>
<td>0.3004</td>
<td>8(2), 13(2), 14(2), 17(2)</td>
</tr>
</tbody>
</table>
38-atom fullerene isomers
Optimized Structures

$Si_{38}$

$Si_{20}$

OTBMD  GTBMD  DFT/B3LYP
Cohesive Energy

![Cohesive Energy Graph]

- **Cohesive Energy (meV)**
- **Isomer number**

Graph showing the cohesive energy as a function of isomer number for two different methods: GTBMD and DFT/B3LYP.
## Comparison between \( \text{Si}_{38} \) and \( \text{Si}_{20} \)

### Cohesive energy

<table>
<thead>
<tr>
<th>Method</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTBMD</td>
<td>0.1171 eV</td>
</tr>
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**Comparison between Si_{38} and Si_{20}**

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</tr>
</tbody>
</table>

Marsen and Sattler assumptions:

- The smallest Si fullerenes are the most stable
- For Si a fused pentagon rule can replace the IPR of C fullerenes

Bond Lengths

![Graph showing bond length thresholds for Si$_{38}$ and Si$_{20}$ with different methods: OTBMD, GTBMD, and DFT/B3LYP.](image)
Sum of the three bond associated angles for ideal cases

For \( n_p \) pentagons (\( n_p = 0, 1, 2, 3 \))
\[
\text{sum} = 360^\circ - 12^\circ n_p
\]

- 3 hexagons: \( 360^\circ \)
- 2 hexagons + 1 pentagon: \( 348^\circ \)
- 1 hexagon + 2 pentagons: \( 336^\circ \)
- 3 pentagons: \( 324^\circ \)
- Tetrahedral arrangement: \( 328.41^\circ \)
- Not hybridized bonding: \( 270^\circ \)
Distribution of the sum of the three bond associated angles
Acknowledgments

• Prof. A.N. Andriotis
• This work was partially supported by EU TMR Network "USEFULL"
The Si(110) surface

Si-C nanotubes

M. Menon, E. Richter, A. Mavrandomakis, G. Froudakis, and A. N. Andriotis,
Si nanowires and nanotubes

Si fullerene-like endohedral clusters

Q. Sun, Q. Wang, P. Jena, B. K. Rao, and Y. Kawazoe,
Si clathrates

Si20

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