Does N violate the isolated pentagon rule?

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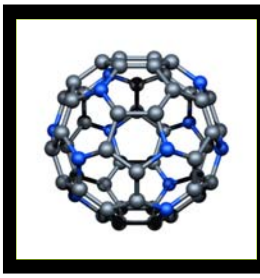
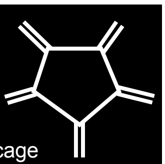
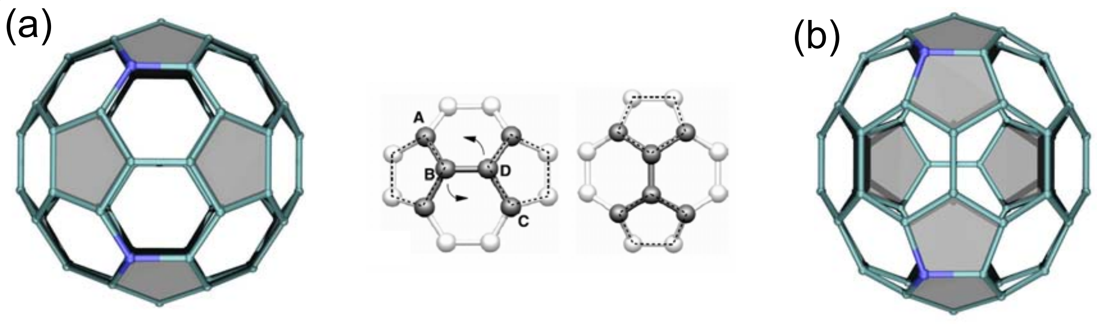


- ‘Classic’ model of $C_{48}N_{12}$ has one N per pentagon
- Claimed to form in *fullerene-like* thin films grown by magnetron sputtering, at centre of N-rich carbon onions.
- Many C/N species seen in mass spectrometry of arc-electric graphite with pyrrole / N_2 / NH_3.
- *Is this model right?*



Isolated Pentagon Rule (IPR)
Pentagons repel each other!

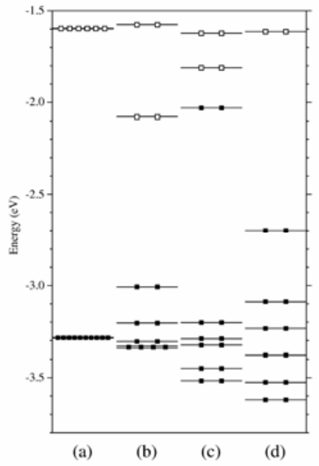
- Obeyed in fullerenes, nanotubes, nanohorns, etc.
- Why C_{60} is most stable fullerene – smallest closed cage with pentagons separated.
- Pentagon bonds ‘single’ character; neighbouring pentagons have under-coordinated shared carbon atoms.



$C_{58}N_2$ (a) before and (b) after the central hexagon bond is rotated by 90°.
The right hand structure contains two pentagon pairs, and is **more stable** by 0.54eV.
Nitrogen atoms are marked in blue, pentagons are filled in grey.

In classic C_{60} (b) is 1.6eV **less** stable.

Nitrogen stabilises the paired pentagons, and violates the isolated pentagon rule



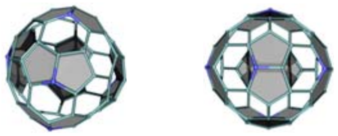
DFT Kohn-Sham eigenvalues in eV around the HOMO-LUMO gap

(a) C_{60}
(b) C_{60} with one bond rotation (2 sets of paired pentagons)
(c) As (a) with two substitutional N atoms
(d) As (b) with two substitutional N atoms, one per paired pentagon.

Black (white) squares show filled (empty) states.

Reason for N stabilisation of paired pentagons:

- In isolated pentagon case, additional N electron forced to occupy high lying anti-bonding state.
- In paired pentagon case, filled level drops. Pentagon pairs become aromatic.



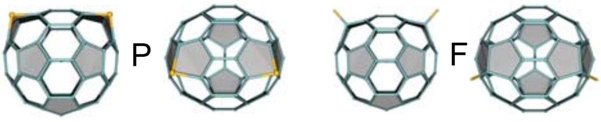
$C_{54}N_6$, two views of the same isomer containing only paired pentagons, each with a single N atom. The pentagons are arranged in two symmetric rows of three. This is **0.85eV more stable** than $C_{54}N_6$ obeying the IPR.

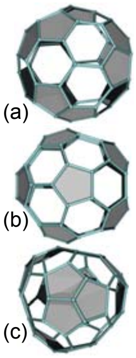
	C_{60}-SW	C_{58}-N_2-SW		Pentalene
r_1	1.458	1.400		1.439
r_2	1.391	1.390	*1.399*	1.355
r_3	1.404	1.398	*1.396*	1.457
r_4	1.451	1.403	*1.427*	1.353
r_5	1.456	1.427	*1.436*	1.474

Calculated bond lengths (Å) for paired pentagons in C_{60}- containing two paired pentagons, and the same unit with a substitutional nitrogen atom at the junction of r_1-r_2-r_3. Italics indicate bonds on the opposite side of the paired pentagon to the nitrogen. Bond r_4 is nearest to the other paired pentagon. In C_{60} we find pentagon bonds of 1.439Å and hexagon bonds of 1.387Å.

Repeating this comparison shows the (b) isomer more stable for X=CH (0.31eV) or CF (0.17eV), but less stable for P (0.18eV) and B (1.06eV).

Since paired pentagon formation only likely during growth, when F and H less likely to bind, suggests N best candidate for growth of stable **paired pentagon fullerenes**.

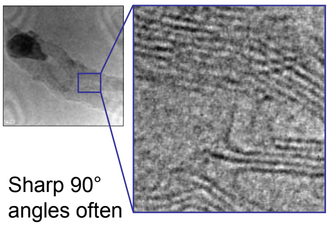




Views of **C_{50}** (a) D_3 (b) D_{5h} and (c) D_3 (two triple pentagon) isomers. The most stable is (a). (b) is 0.19eV less stable, (c) is 3.79eV less stable due to its highly distorted structure.

- With 6N present, (a) most stable by 0.77eV
- With 2N present, (c) now 1.6eV less stable than (a)

→ Nitrogen strongly stabilises paired pentagons, only weakly triplet pentagons.



Sharp 90° angles often seen in PECVD N-doped nanotubes – paired pentagons?

Summary

- N violates the isolated pentagon rule.
- Stabilises azapentalene **paired pentagon** units
- New family of smaller (or larger) azafullerenes possible with different chemistry
- **Implications for N doped carbon nanostructures** (nanotubes, thin films, fullerene-like thin films)
- Paired pentagons allow sharp angles (cf. 90° nanotube tip closure in BN)