stability, chemical structure and Clar's aromatic sextets in graphene hydrogenated edges

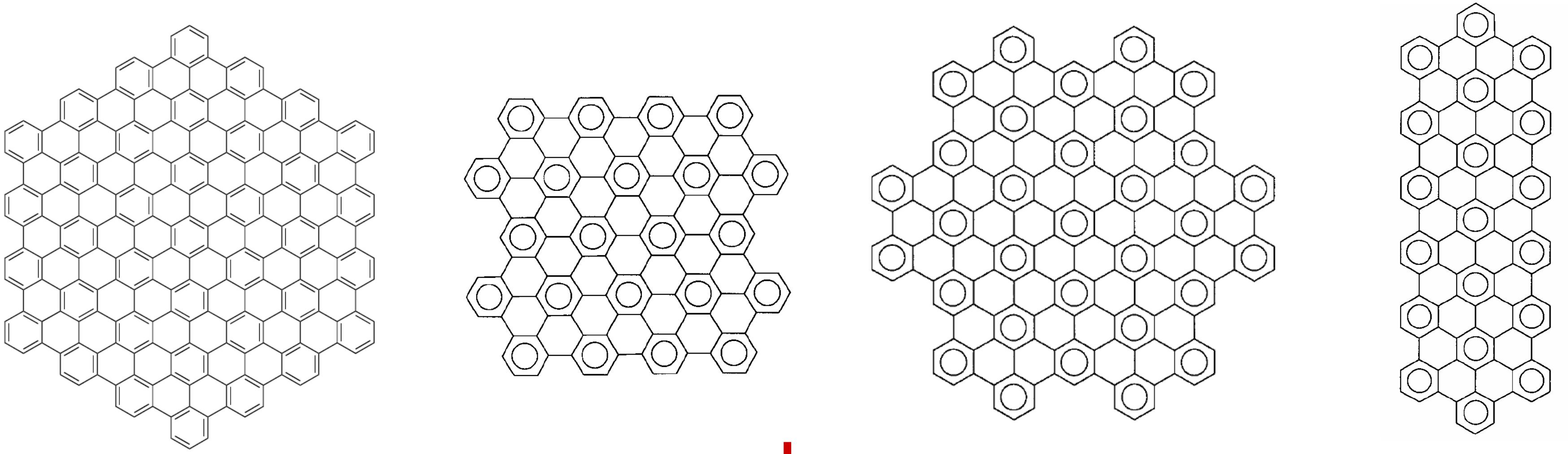
T. Wassmann, A.P. Seitsonen, A.M. Saitta, M. Lazzeri, F. Mauri
IMPMC, Université Pierre et Marie Curie-Paris 6, CNRS

Phys. Rev. Lett. 101, 096402 (2008)

outline

- why graphene and its edges are important?
- stability of edges as a function of H_2 partial pressure
- edge electronic structure
- Clar's sextets an empirical tool to predic stability and electronic structure of edges
- visualisation of Clar's sexted in geometry and STM images

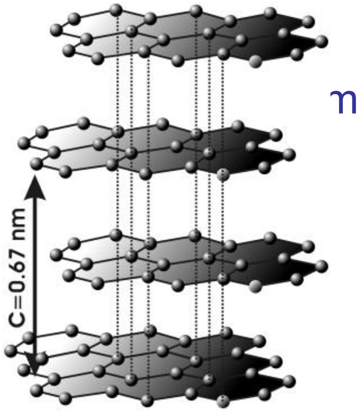
giant polycyclic hydrocarbons



graphene

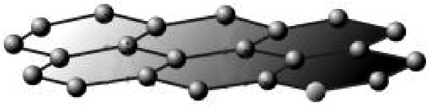
a very giant polycyclic hydrocarbon

graphite

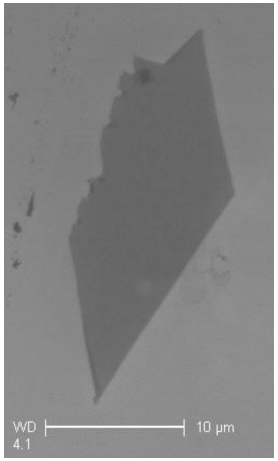


micromechanical
cleavage

graphene



10 μm wide
single layer flake



graphene ribbons vs nanotubes in active devices

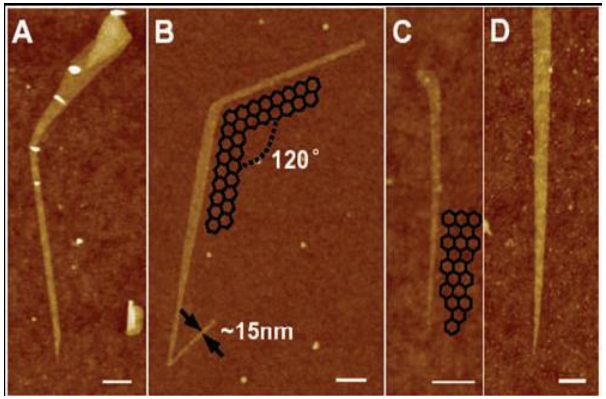
- semiconducting nanotubes:
  - -difficult to position in a massively integrated chips
  - -gap depends on chirality and diameter (to be controlled)
  - -very high mobility

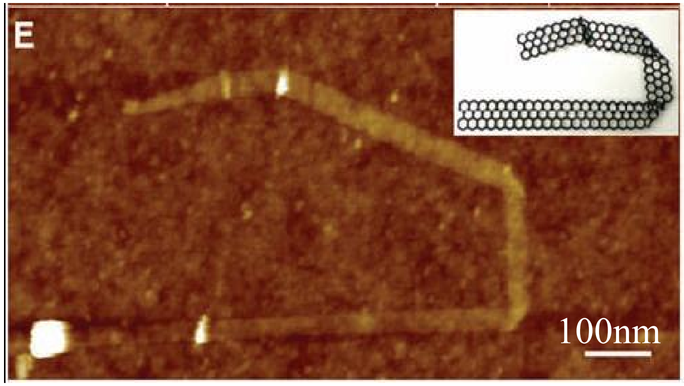
- graphene ribbons:
  - -lithography for massively integrated chips
  - -gap depends on ribbon geometry controlled by lithography
  - -very high mobility requires no defects on the edges

graphene material for post-MOS electronics
if we are able to cut it nicely

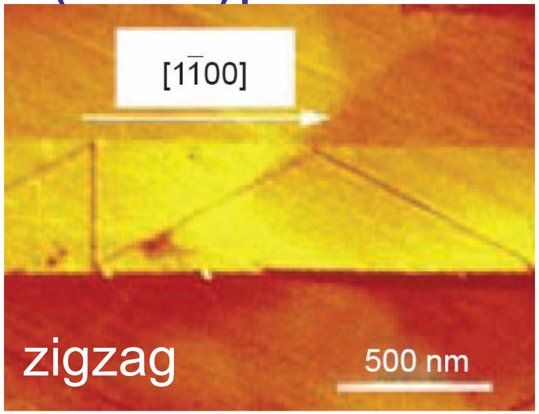
today best cuts

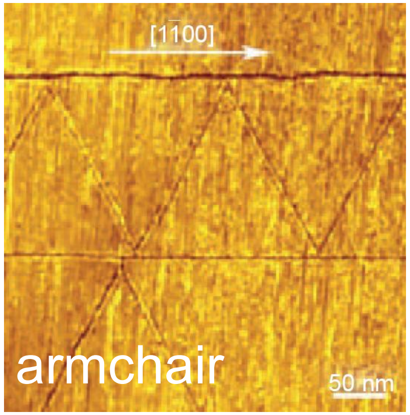
Chemical route (solution-dispersion and sonication): ribbons with lateral width <10nm with regular edges [X. Li et al., Science 319, 1229 (2008); X. Wang et al., PRL 100, 206803 (2008)]

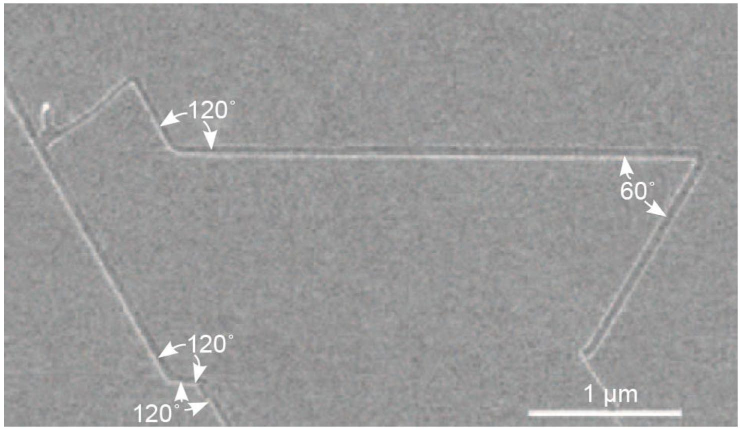




Thermally activated nanoparticle etching in H_2 atmosphere [S. Datta et al. Nano Lett. 8, 1912 (2008); L. Ci et al. Nano Res. 1, 116 (2008)]

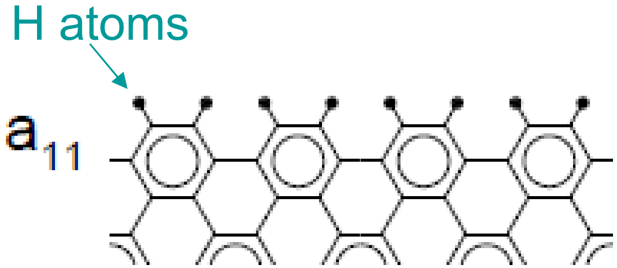






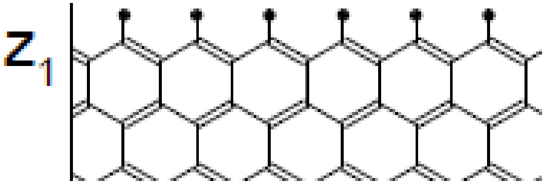
prototype edges discussed in literature

- armchair monohydrogenated edge:



- zigzag monohydrogenated edge:

ferromagnetic (in ribbons antiferromagnetic coupling between the two edges)

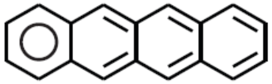


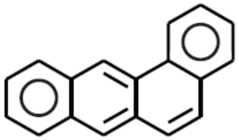
-are these the correct prototypes?

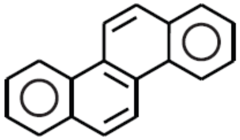
-which regular edges are expected in experiments?

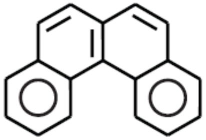
-how can we recognize experimentally such edges?

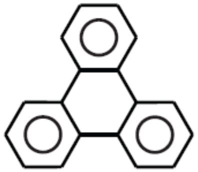
structure and stability of polycyclic hydrocarbon from DFT first principles calculations
PBE vs. B3LYP


1


2


3


4


5

Energy differences (in eV)

Molecule	PBE	B3LYP/6-31G*	Exp.
Naphthacene **1**	0.40	0.44	0.40
Benz[a]anthracene **2**	0.08	0.08	0.26
Chrysene **3**	0.00	0.00	0.00
Benzo[c]phenanthrene **4**	0.24	0.26	0.29
Triphenylene **5**	0.03	0.03	0.02

structure and stability of hydrogenated edges from DFT first principles calculations

ribbon calculations with PBE-GGA functional, plane-waves and pseudopotentials, Quantum-espresso package

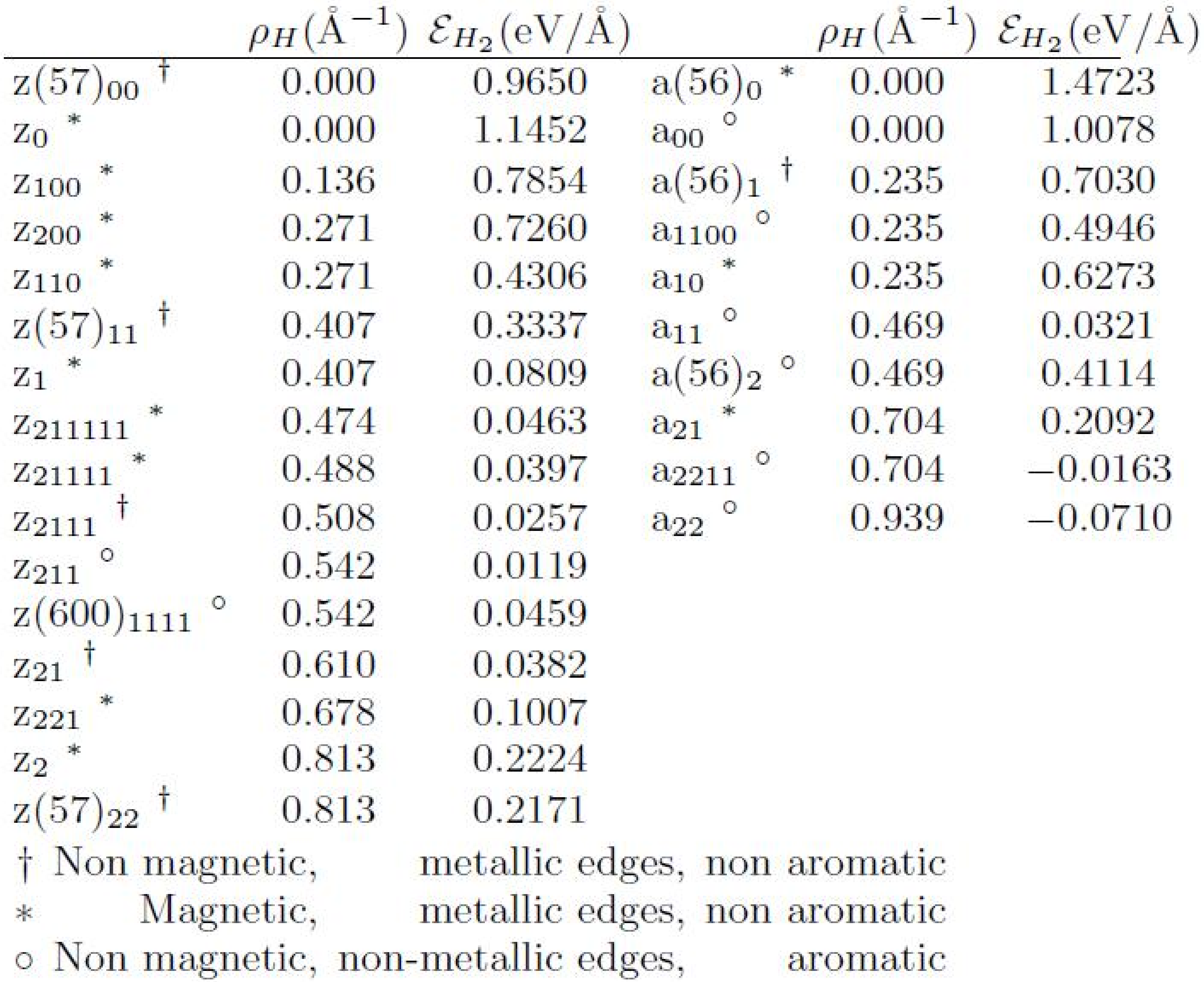
$$\text{edge energy per unit length} = \mathcal{E}_{H_2} = \frac{1}{2L}\left(\overset{\substack{\text{ribbon}\\ \text{energy}\\ \downarrow}}{E^{ribb}} - \underset{\substack{\nwarrow\\ \text{C atoms}\\ \text{ribbon}}}{N_C}\,\overset{\substack{\text{C energy}\\ \text{bulk graphene}\\ \downarrow}}{E^{blk}} - \underset{\substack{\nwarrow\\ \text{H atoms}\\ \text{ribbon}}}{\frac{N_H}{2}}\,\overset{\substack{H_2\\ \text{energy}\\ \downarrow}}{E_{H_2}}\right)$$

$$\text{hydrogen per unit length} = \rho_H = N_H/(2L)$$

For a given molecular hydrogen chemical potential μ_{H_2}, the most stable edge minimizes the free energy:

$$G_{H_2} = \mathcal{E}_{H_2} - \rho_H \mu_{H_2}/2$$

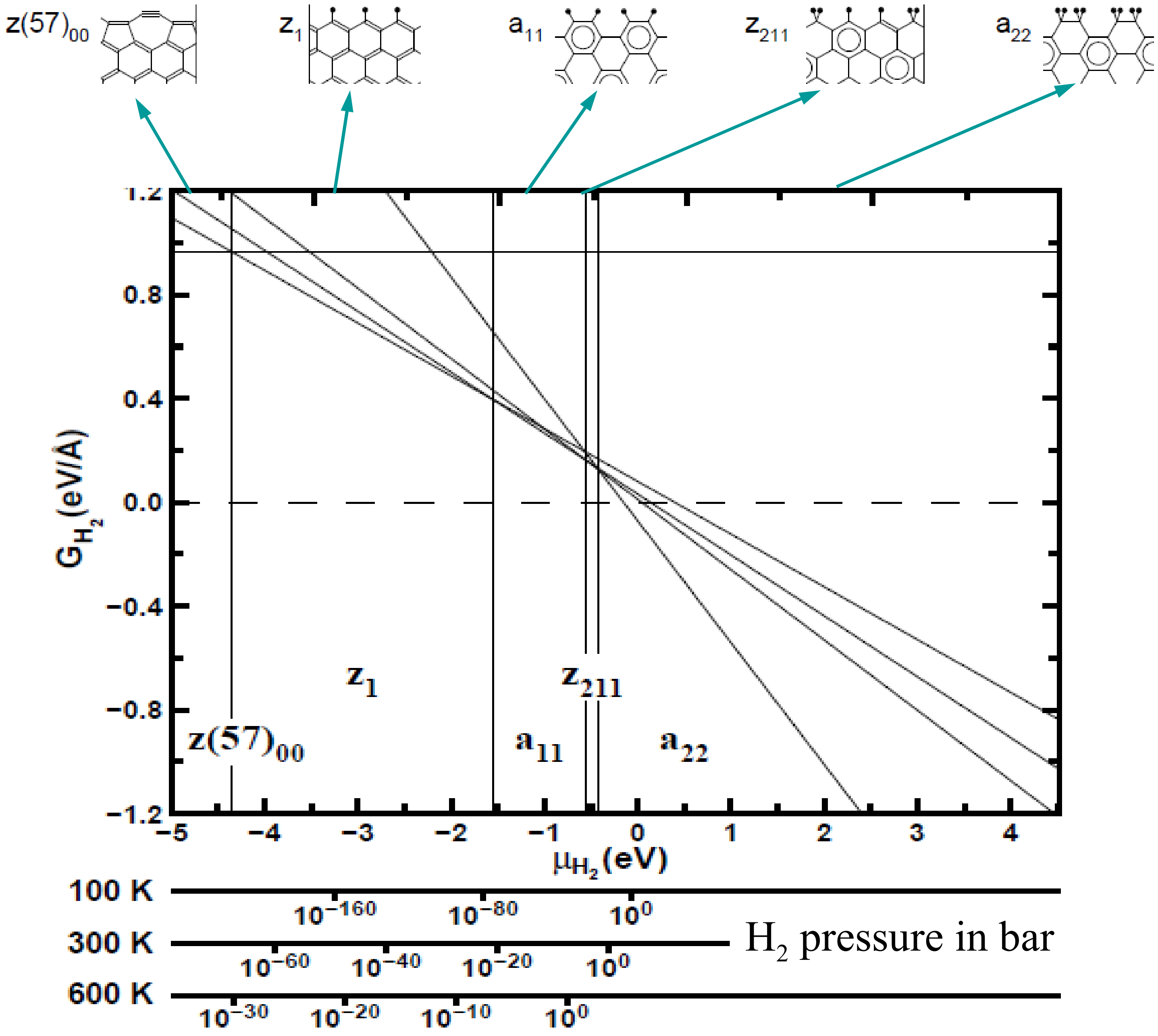
our theoretical database (26 structures)



	$\rho_H(\text{Å}^{-1})$	$\mathcal{E}_{H_2}(\text{eV}/\text{Å})$		$\rho_H(\text{Å}^{-1})$	$\mathcal{E}_{H_2}(\text{eV}/\text{Å})$
$z(57)_{00}$ †	0.000	0.9650	$a(56)_0$ *	0.000	1.4723
z_0 *	0.000	1.1452	a_{00} ○	0.000	1.0078
z_{100} *	0.136	0.7854	$a(56)_1$ †	0.235	0.7030
z_{200} *	0.271	0.7260	a_{1100} ○	0.235	0.4946
z_{110} *	0.271	0.4306	a_{10} *	0.235	0.6273
$z(57)_{11}$ †	0.407	0.3337	a_{11} ○	0.469	0.0321
z_1 *	0.407	0.0809	$a(56)_2$ ○	0.469	0.4114
z_{211111} *	0.474	0.0463	a_{21} *	0.704	0.2092
z_{21111} *	0.488	0.0397	a_{2211} ○	0.704	−0.0163
z_{2111} †	0.508	0.0257	a_{22} ○	0.939	−0.0710
z_{211} ○	0.542	0.0119			
$z(600)_{1111}$ ○	0.542	0.0459			
z_{21} †	0.610	0.0382			
z_{221} *	0.678	0.1007			
z_2 *	0.813	0.2224			
$z(57)_{22}$ †	0.813	0.2171			

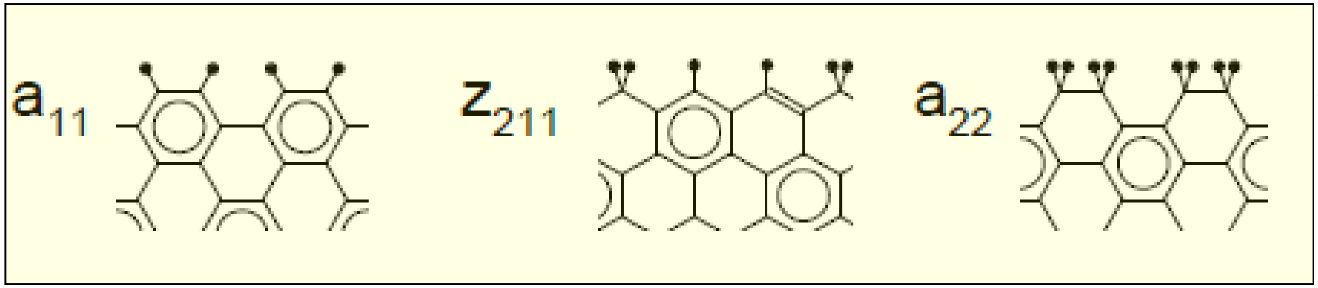
† Non magnetic, metallic edges, non aromatic
* Magnetic, metallic edges, non aromatic
○ Non magnetic, non-metallic edges, aromatic

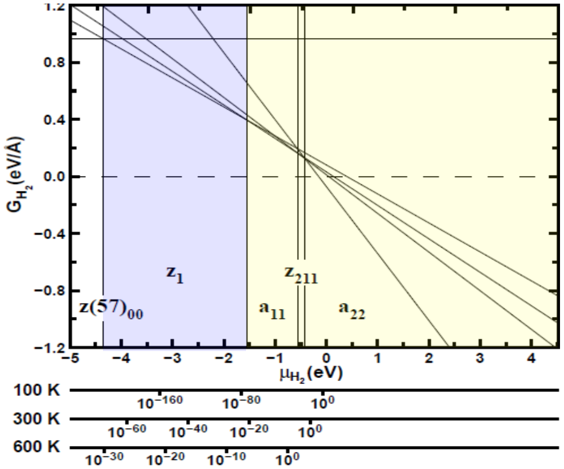
the most stable hydrogenated edges



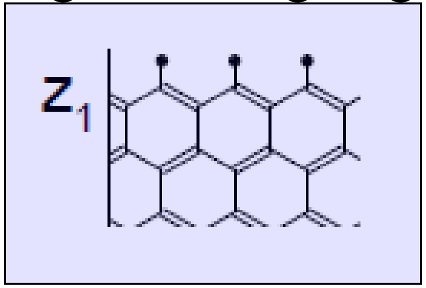
the most stable hydrogenated edges

- At standard conditions: 300K, P_{H_2}> 10x10^{-20} bar (in air P_{H_2}= 5x10^{-7} bar) the stable edges are:



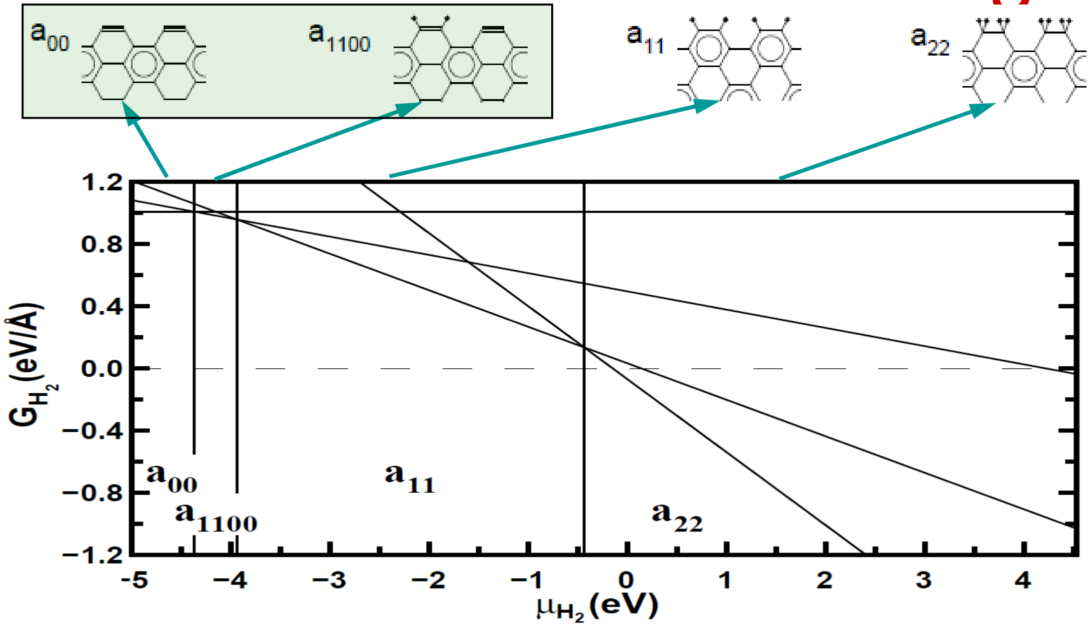


- Monohydrogenated magnetic zigzag stable only in ultra vacuum



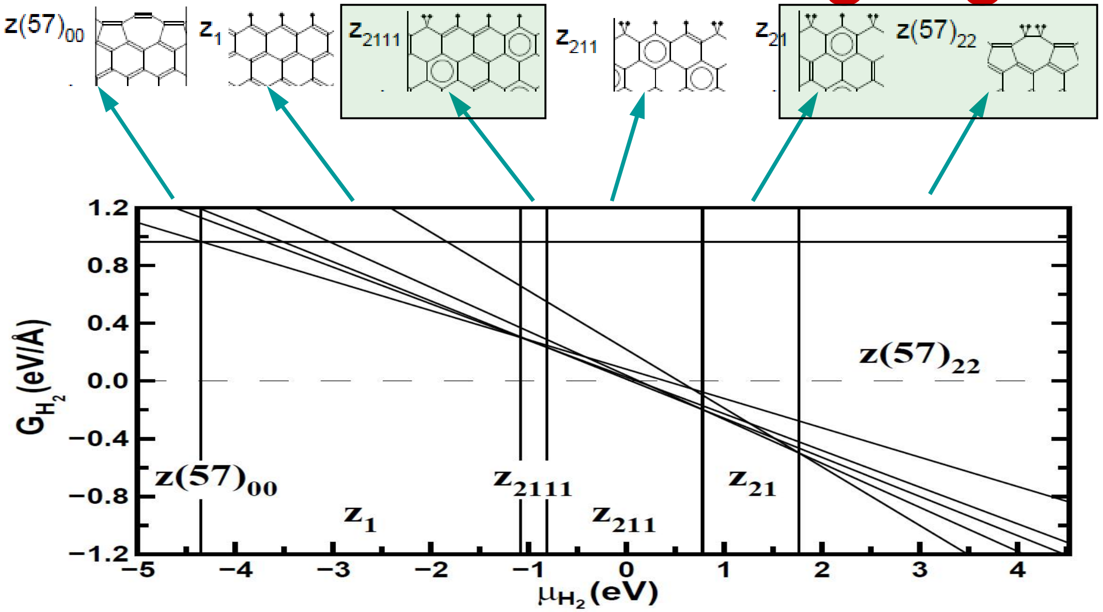
- At high hydrogen pressure (μ_{H_2}~0) the free energy is negative: graphene spontaneously breaks to from ribbons as observed in [X. Li et al., Science 319, 1229 (2008)]

the most stable armchair edges



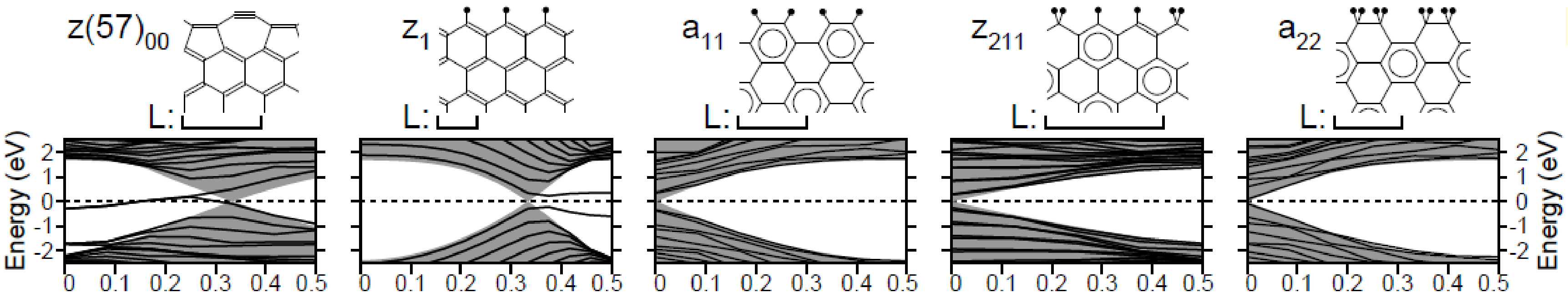
other edges

the most stable zigzag

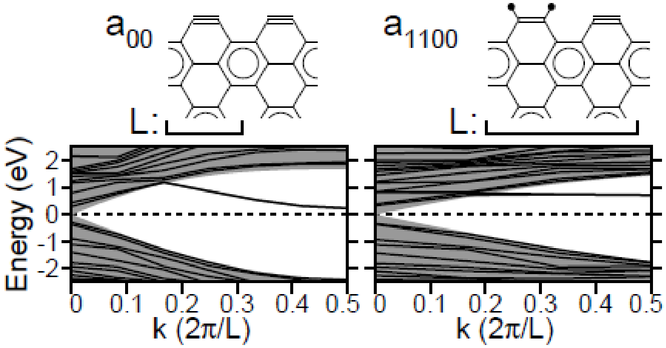


edge electronic-structure

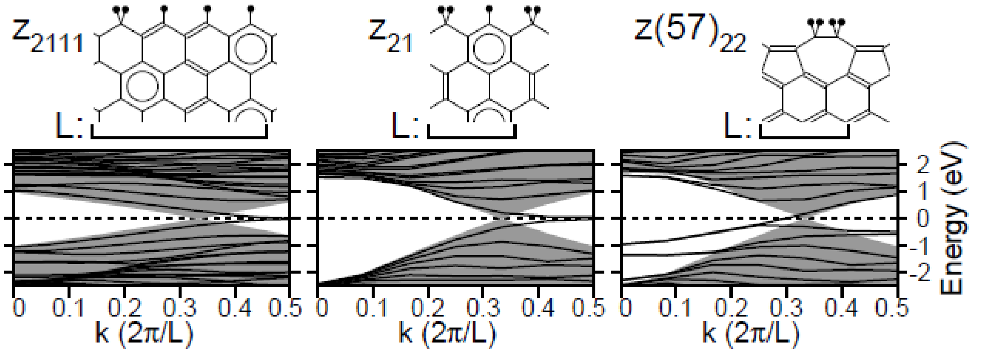
most stables edges



other armchair edges

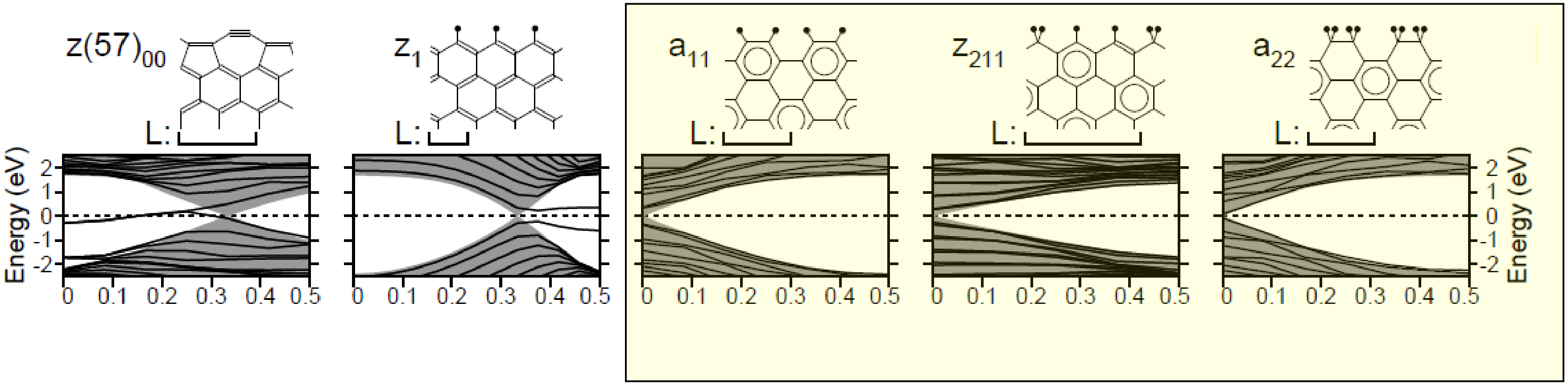


other zigzag edges



edge electronic-structure

most stables edges



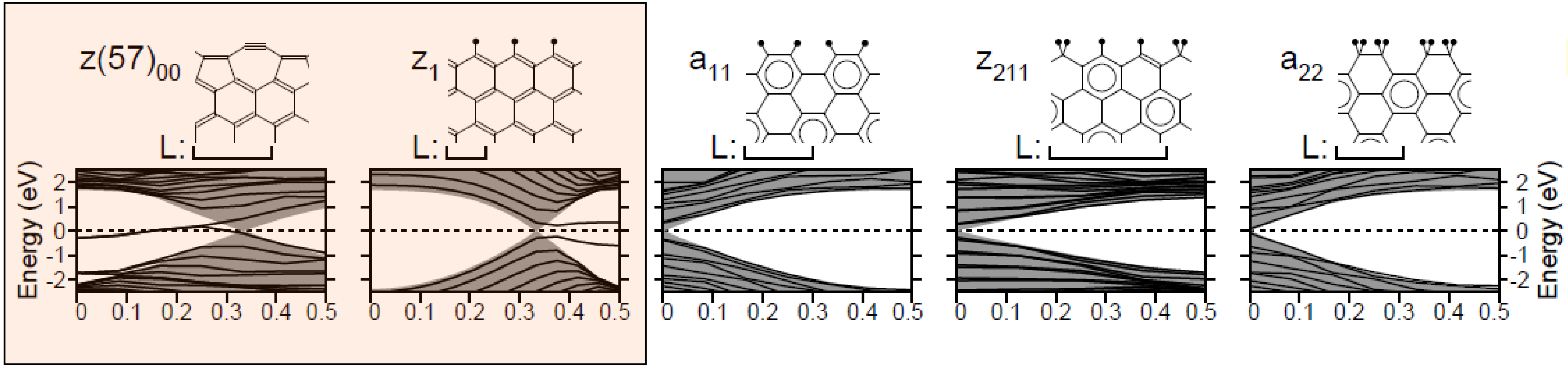
the most stable edges at normal conditions (a_{11}, z_{211}, a_{22}):

- do not have edge states (electron states localized at the edge) in agreement with the observation of a gap in gated ribbons in [PRL. 100, 206803 (2008)].

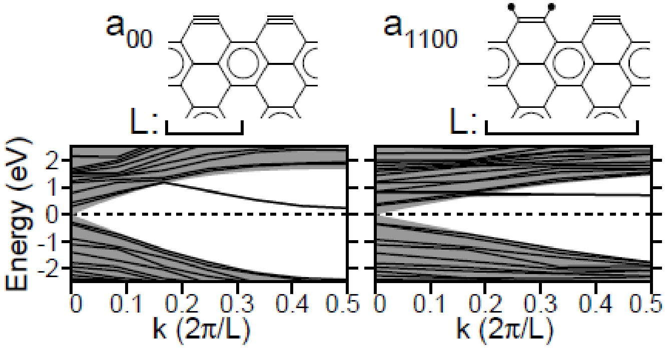
- in absence of edge states available for chemical bonding, they should be chemically inert and meta-stable outside their stability region

edge electronic-structure

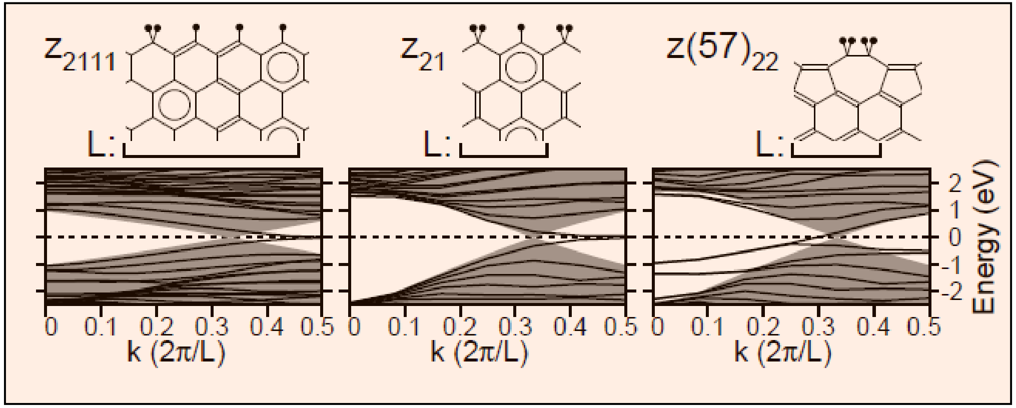
most stables edges



other armchair edges



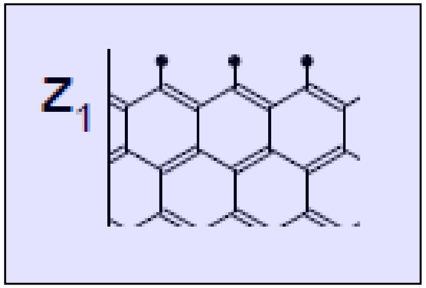
other zigzag edges

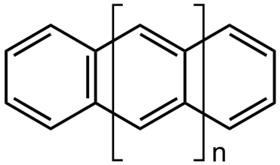


metallic edges:

- an edge state crosses the Fermi energy
- z_1 is metallic in the non-magnetic phase, but a gap is opened in finite ribbons by antiferromagnetic ordering

instability and reactivity of the monohydrogenated zigzag edge z_1

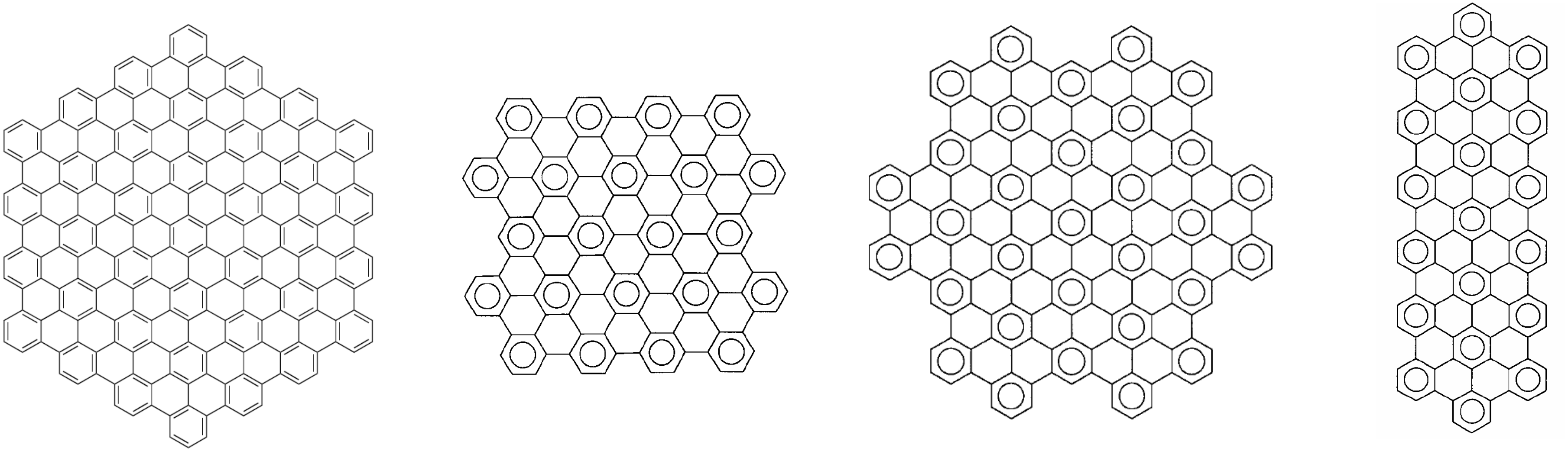




- the acenes are prototypes of the z_1 ribbons

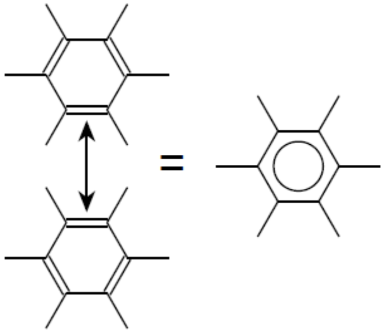
$n < 5$ stable, $n = 5,6$ very reactive, $n > 6$ unstable

- giant polycyclic hydrocarbons do not have z_1 edges:



Aromaticity and the Clar's sextet

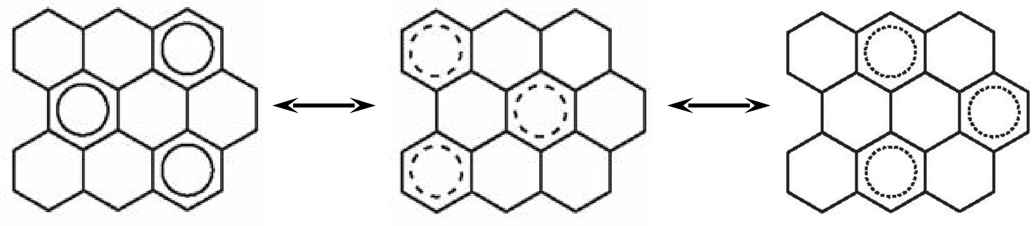
-benzenoid aromatic ring (Clar's sextet) has two resonances:



- a structure with n benzenoid rings has 2^n resonances

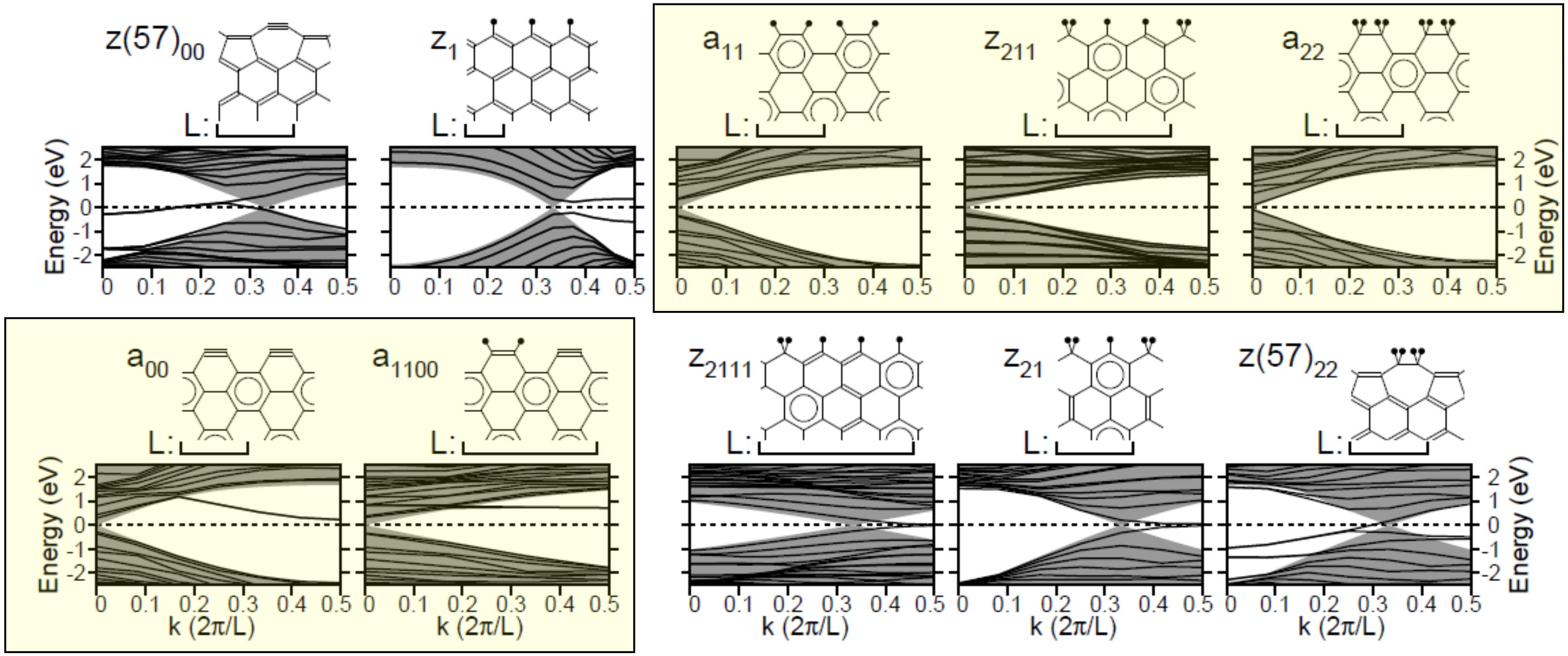
-stability increases with the number of resonances. The most stable isomers maximize the number of benzenoid rings

-a fully aromatic structure has only benzonoid rings (no isolated double bonds). Bulk graphene is fully aromatic:



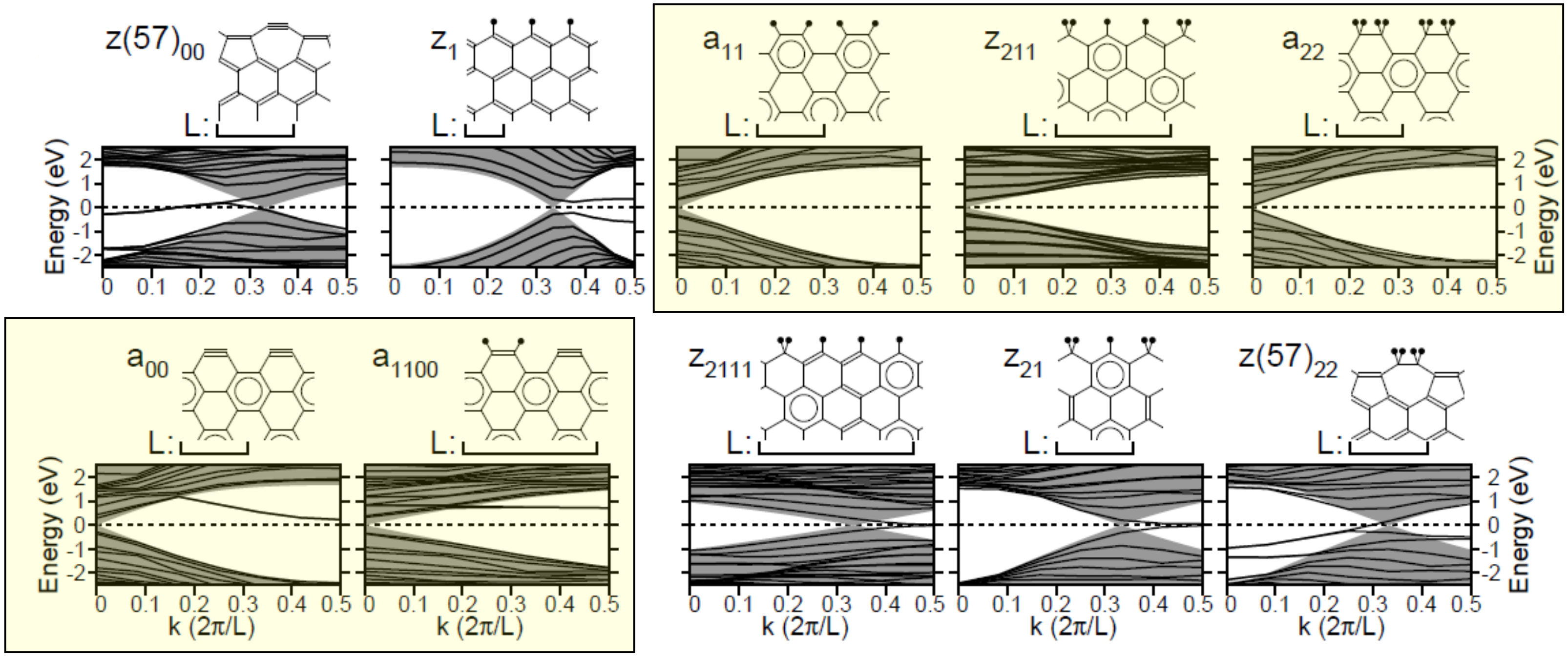
Aromaticity and the Clar’s sextet

-we define as “aromatic edges” those having a density of benzenoid rings of 1/3 compatible with that of the bulk.



Aromaticity and the Clar's sextet

-we define as "aromatic edges" those having a density of benzenoid rings of 1/3 compatible with that of the bulk.

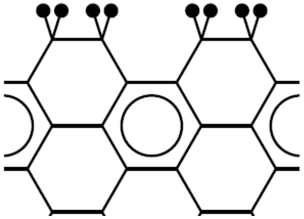


two empirical rules (verified on 26 structures):

- for a given H density, the most stable edges are aromatic (if an aromatic structure exists at such density)

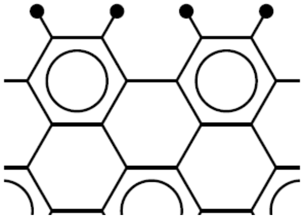
- all the non-aromatic edges are metallic/magnetic and viceversa

aromatic vs. non-aromatic edges



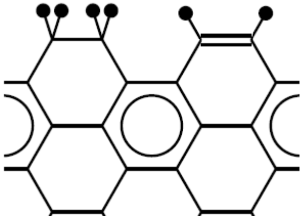
aromatic
non-magnetic
non-metallic

+



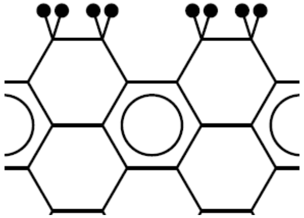
aromatic
non-magnetic
non-metallic

=



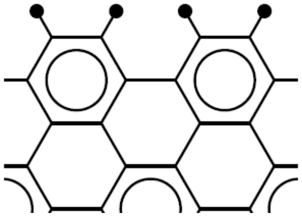
aromatic
non-magnetic
non-metallic

-0.003 eV/Å



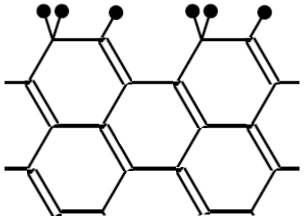
aromatic
non-magnetic
non-metallic

+



aromatic
non-magnetic
non-metallic

=



non-aromatic
magnetic

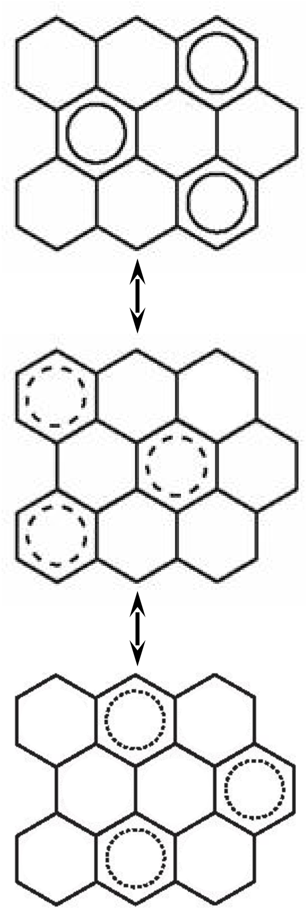
-0.229 eV/Å

Clar's sextet in the geometry and STM images

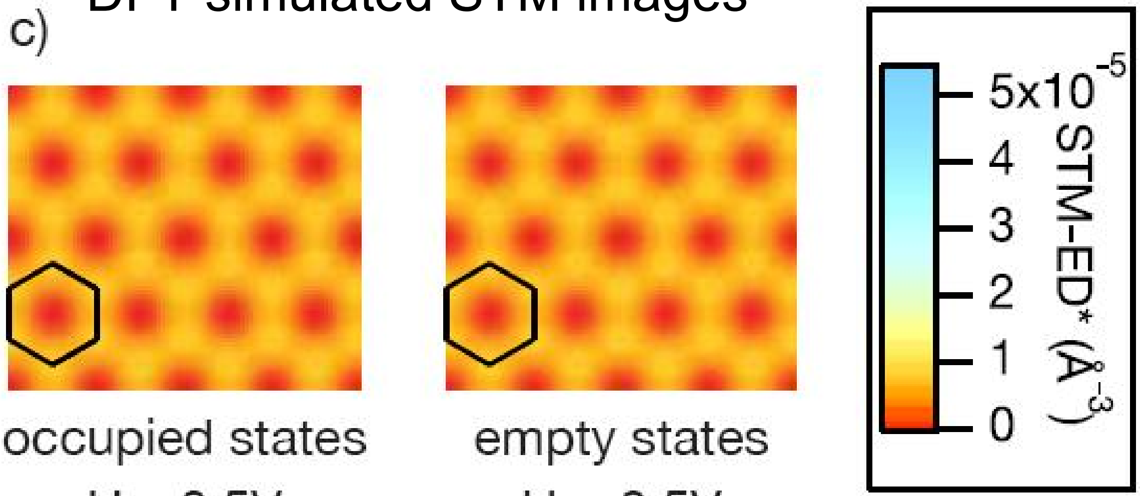
bulk graphene

supeposition of 3 benzonoid structures, all hexagons equivalent

bonding structure



DFT simulated STM images



occupied states

U=–0.5V

empty states

U=+0.5V

STM: electronic states in a window between ε_F and $\varepsilon_F + eU$

$$\mathrm{I}(x,y,z=d,U) \propto \sum_{\mu} |\Psi_{\mu}(x,y,z=d)|^2 \left[f(\varepsilon_{\mathrm{F}} - \varepsilon_{\mu}) - f(\varepsilon_{\mathrm{F}} + eU - \varepsilon_{\mu}) \right]$$

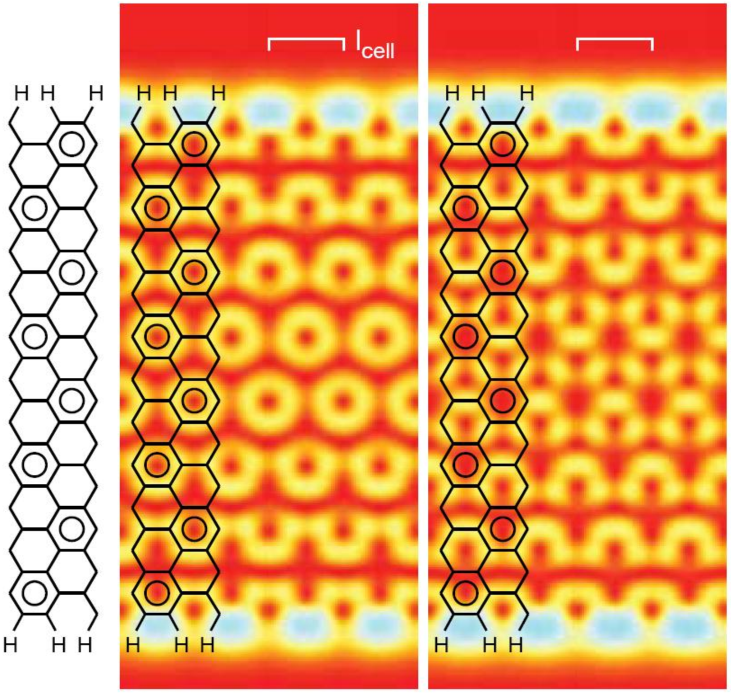
$$d = 3\,\text{Å}$$

Clar’s sextet in the STM images (theory)

CLASS 1

one dominating Clar’s formula maximizing the number of rings

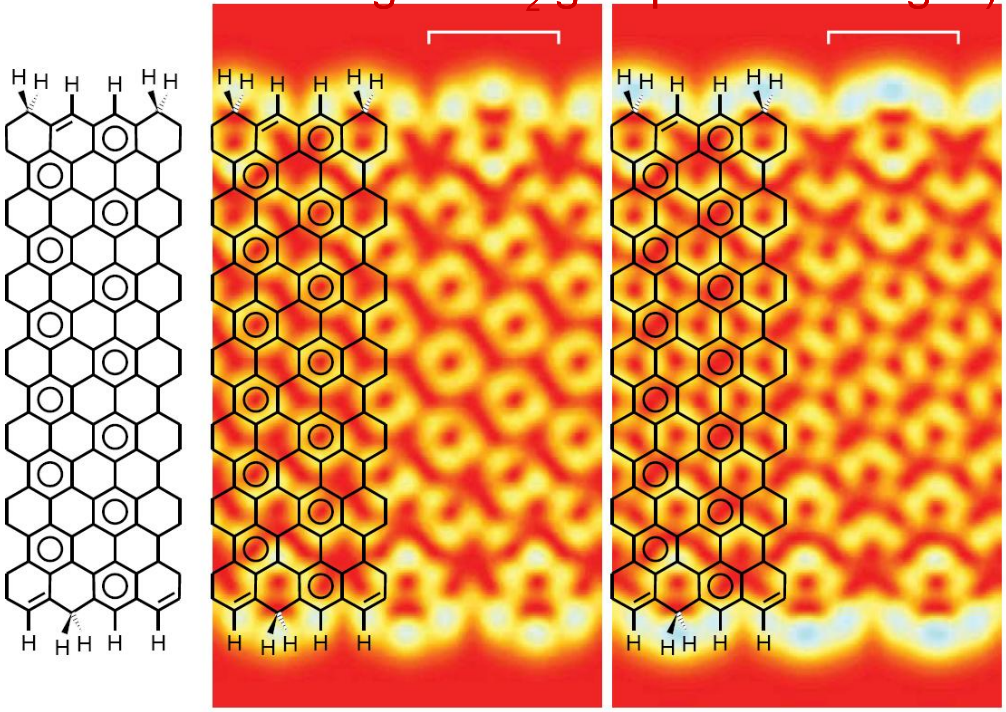
a_{11} ribbons (width 2n+1 exagons)



occupied states
U=−0.5V

empty states
U=+0.5V

z_{211} ribbons (width 2n+2 exagons
non-aligned H_2 groups in two edges)



occupied states
U=−0.5V

empty states
U=+0.5V

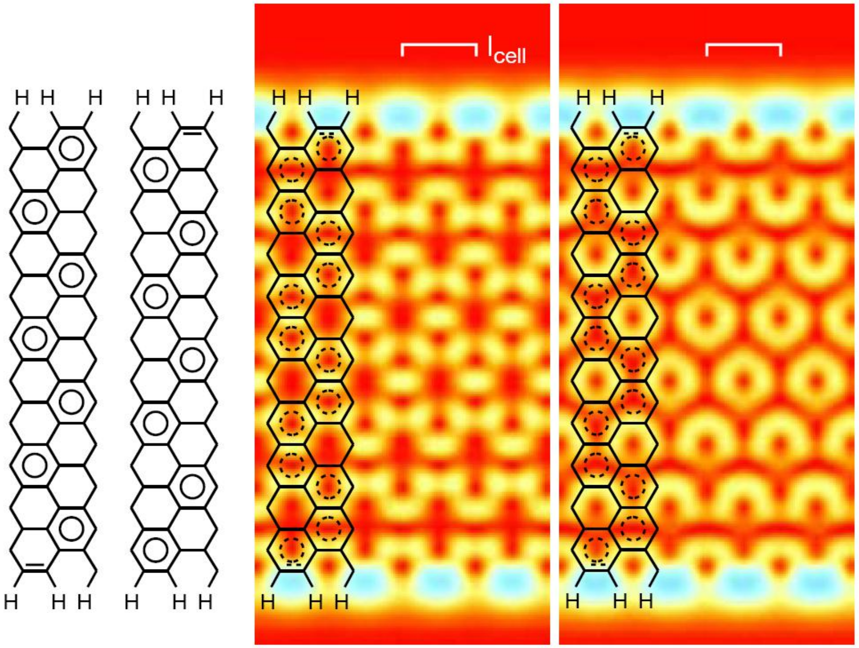
$(\sqrt{3}\times\sqrt{3})R30^\circ$ reconstruction:
rings in occupied-state-images where Clar-sextets are present

Clar’s sextet in the STM images (theory)

CLASS 2

two dominating Clar’s formulae maximizing the number of rings

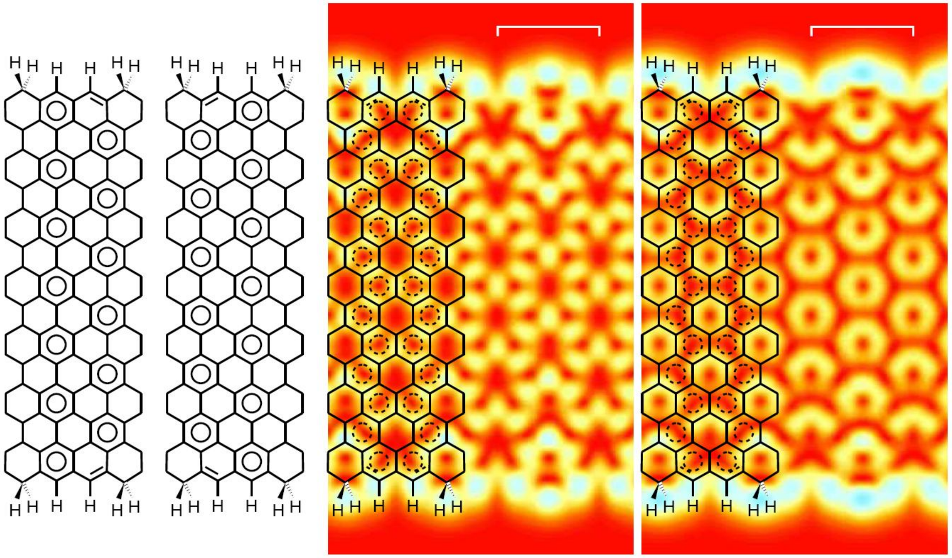
a_{11} ribbons (width 2n+2 hexagons)



occupied states
U=−0.5V

empty states
U=+0.5V

z_{211} ribbons (width 2n+2 hexagons
aligned H_2 groups on two edges)



occupied states
U=−0.5V

empty states
U=+0.5V

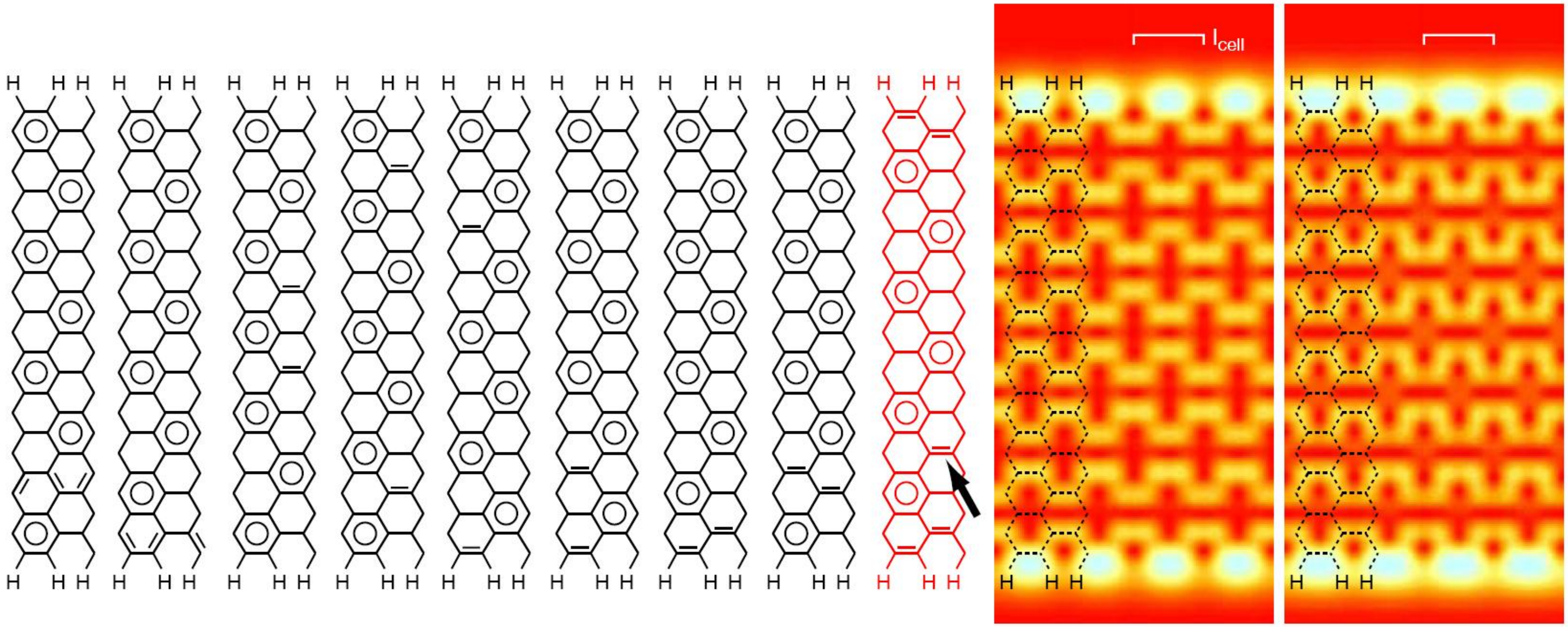
$(\sqrt{3}\times\sqrt{3})R30^\circ$ reconstruction:
rings in empty-state-images where no Clar-sextets are present

Clar’s sextet in the STM images (theory)

CLASS M

many dominating Clar’s formulae maximizing the number of rings

a_{11} ribbons (width 2n hexagons)



occupied states
U=−0.5V

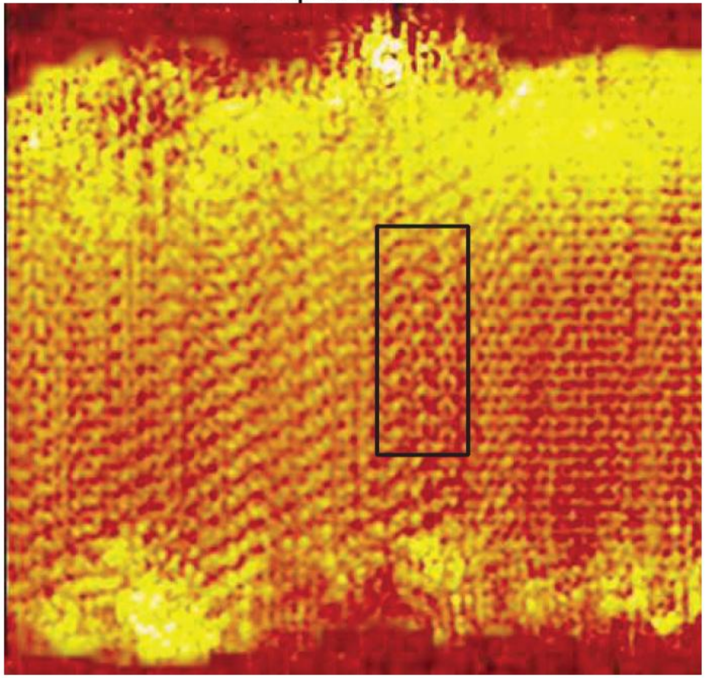
empty states
U=+0.5V

Clar’s sextet in the STM images (experiment)

CLASS 2

rings in empty-state-images

Experiment:



From Figure S3 of the supplementary informations on Nature Nanotechnology 3, 397 - 401 (2008)

Our theoretical result:

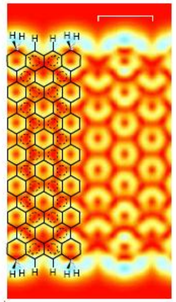


Figure 7c of the manuscript, zigzag orientation

Clar’s sextet in the STM images (experiment)

CLASS M

Experiment:

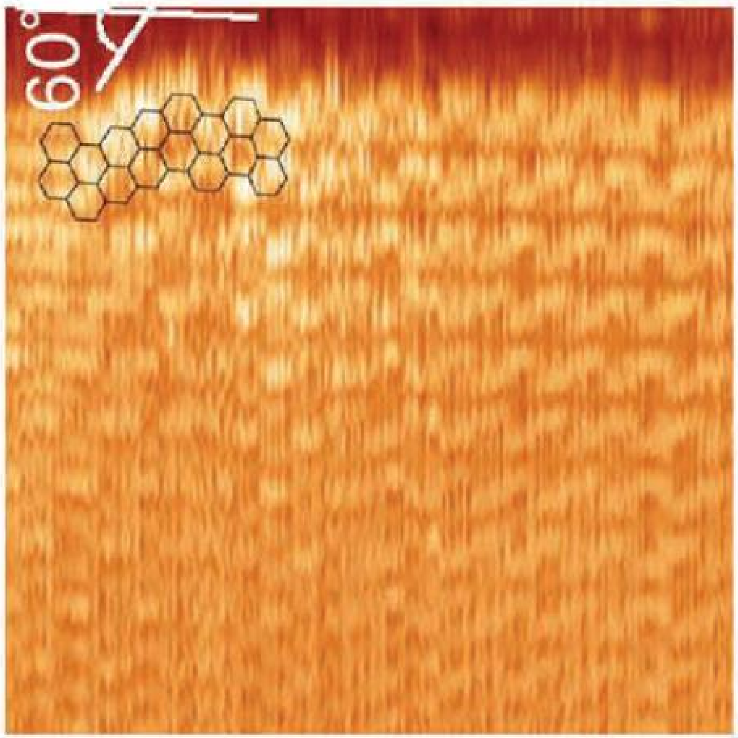


Figure 4b of Phys. Rev. B 73, 125415 (2006)
(rotated by 90°)

Our theoretical results:

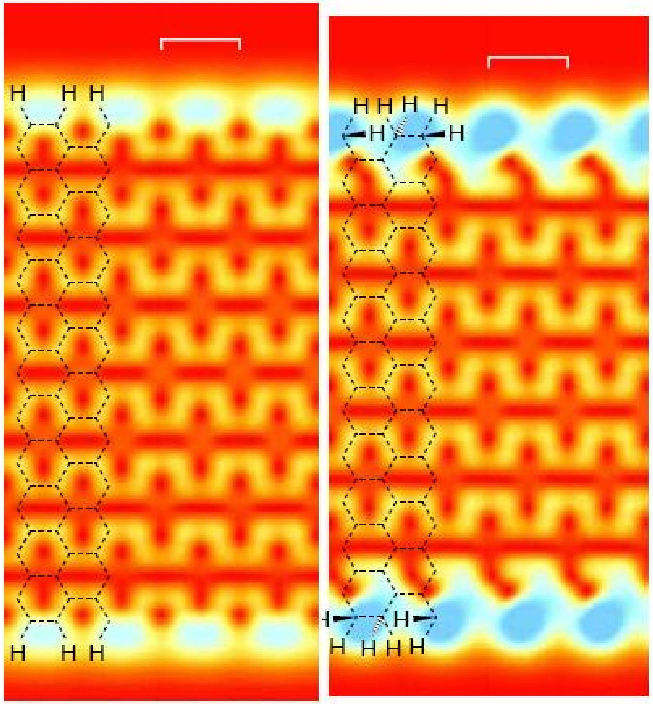
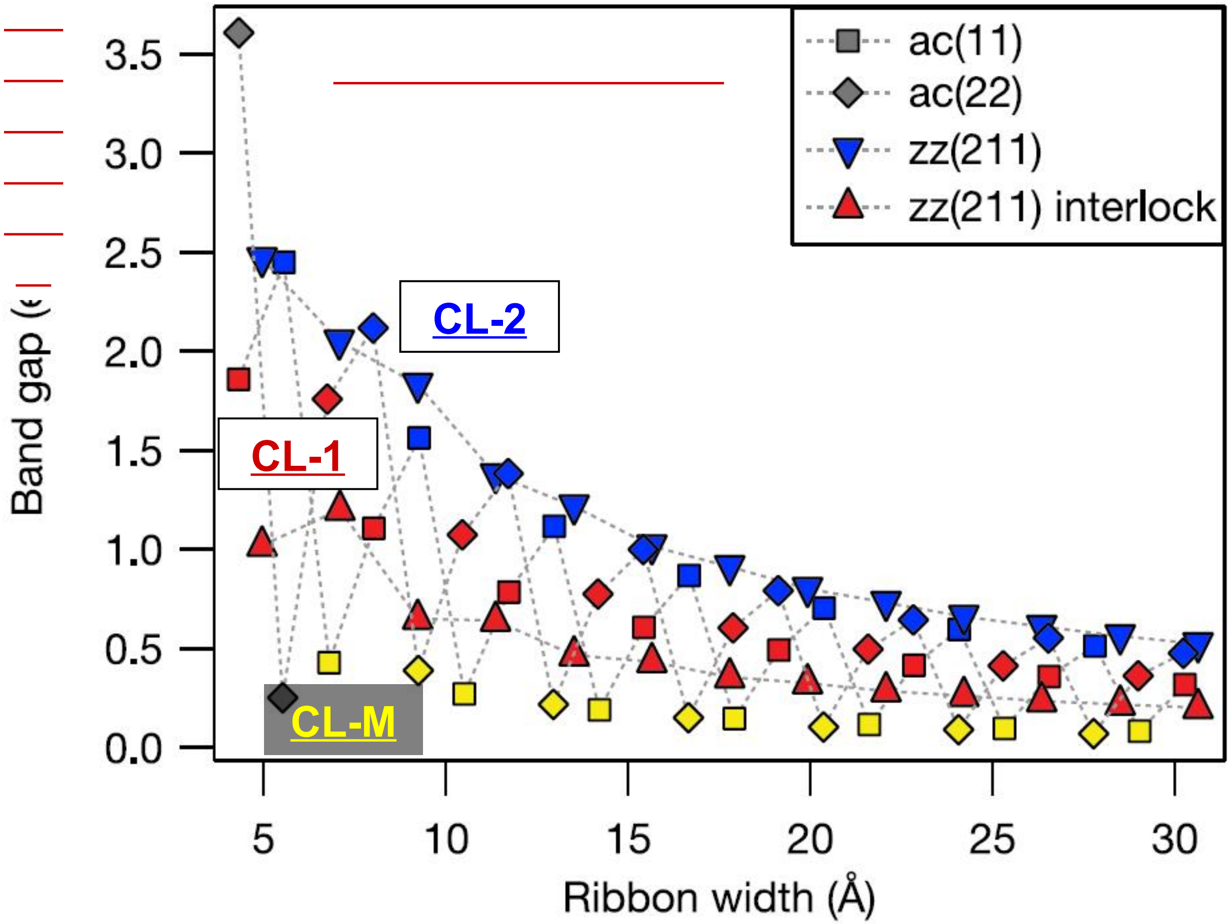


Figure 8a and 8b of the manuscript

DFT Gap energy vs. CLASS

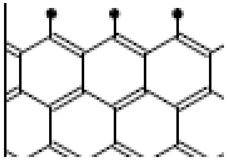
CLASS 1 (one Clar's formula): intermediate energy gaps
CLASS 2 (two Clar's formulae): large energy gaps
CLASS M (many Clar's formulae): small energy gaps



conclusions

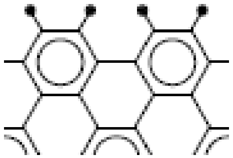
- magnetic zigzag edge stable in ultra-vacuum:

z_1

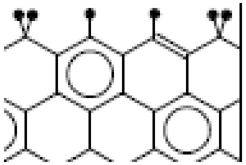


- at standard conditions the stables edges are non-metallic and non-magnetic:

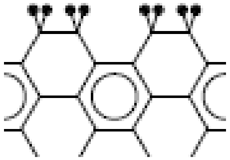
a_{11}



z_{211}



a_{22}



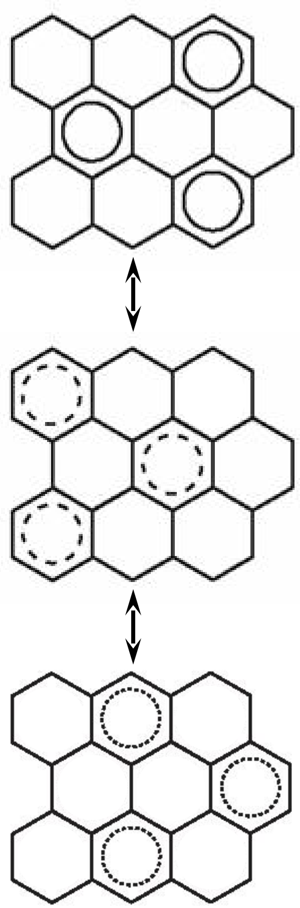
- Clar's formula allows us, also with other functional terminations:
  - to guess, before calculations, the most stable structures
  - to predict the metallic and/or magnetic character of the edges
  - to predict: most stable edges are nonmetallic and nonmagnetic
- fully aromatic ribbons can be divided in 3 classes with similar electronic properties
- Clar's formula visible in STM images:
  - STM can be used to identify the class (structure + edge width)

Clar's sextet in the geometry and STM images

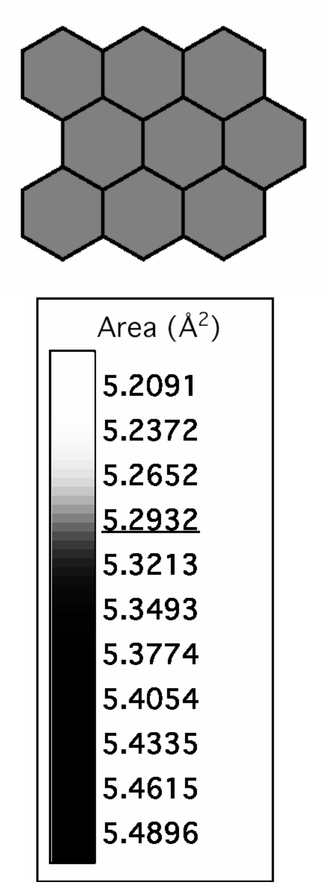
bulk graphene

supeposition of 3 benzonoid structures, all hexagons equivalent

bonding structure



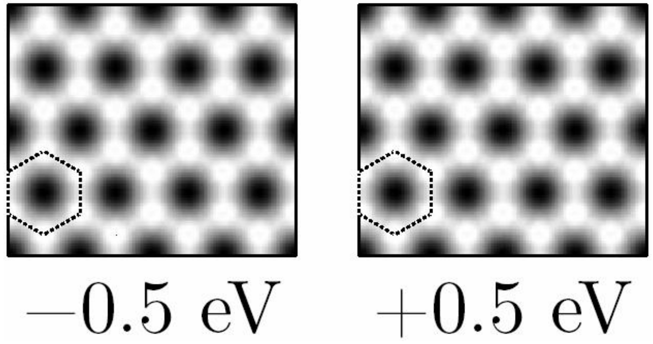
hexagon area



DFT simulated

STM occup. states

STM empty states

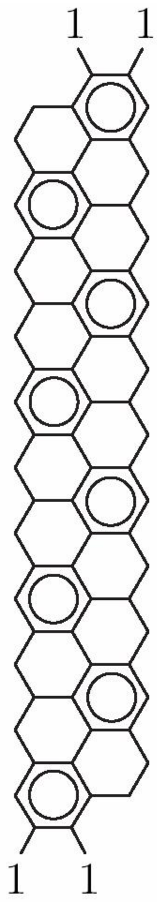


Clar's sextet in the geometry and STM images

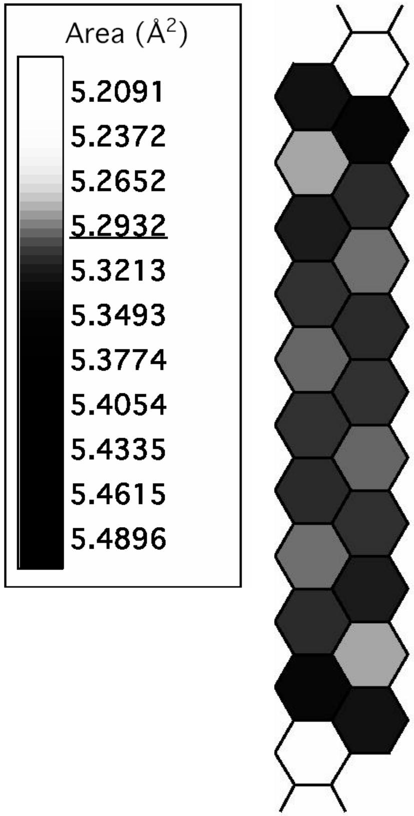
a_{11} ribbon

one dominating Clar's formula maximizing the number of rings

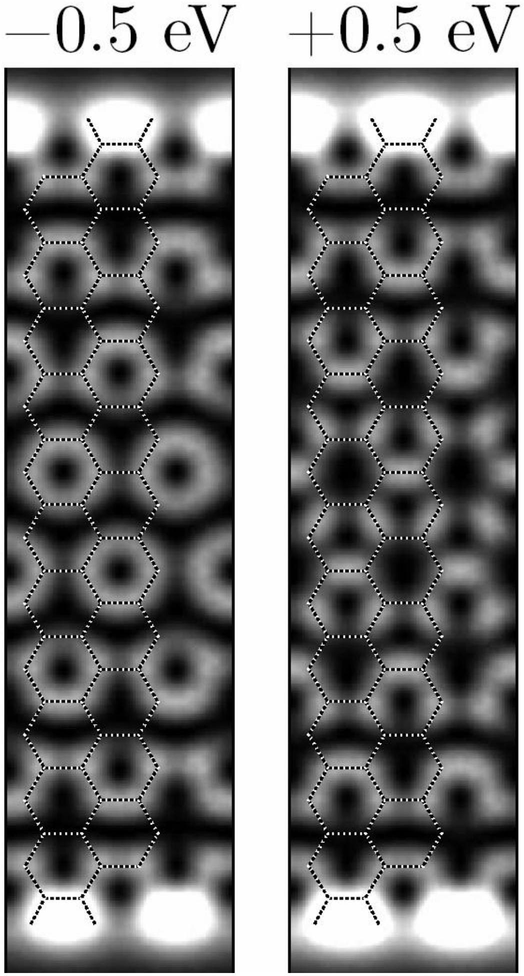
bonding structure



hexagon area



STM

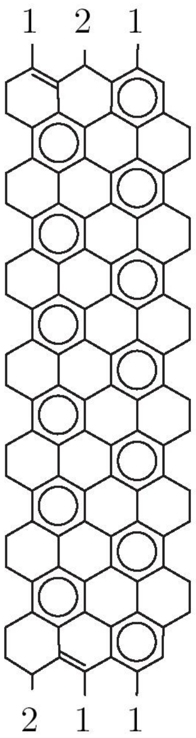


Clar’s sextet in the geometry and STM images

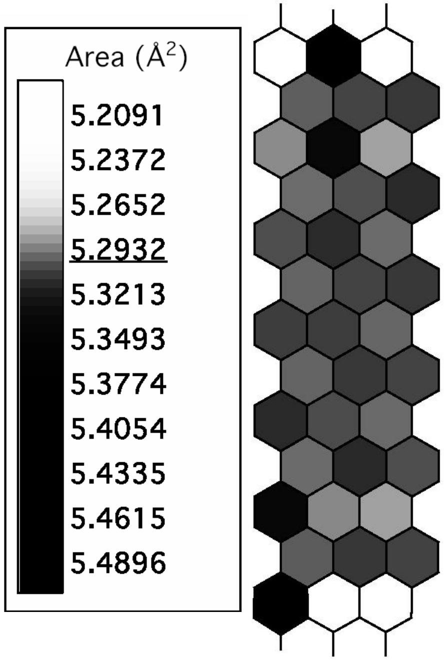
z_{211} ribbon

one dominating Clar’s formula maximizing the number of rings

bonding structure



hexagon area



STM