FAPESP WEEK – 2017: PROPOSAL SPRINT FAPESP/TTU (2015-2017)

Excited States, Poliradical Character and Defects in Polyaromatic Hydrocarbons Systems

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Project Members

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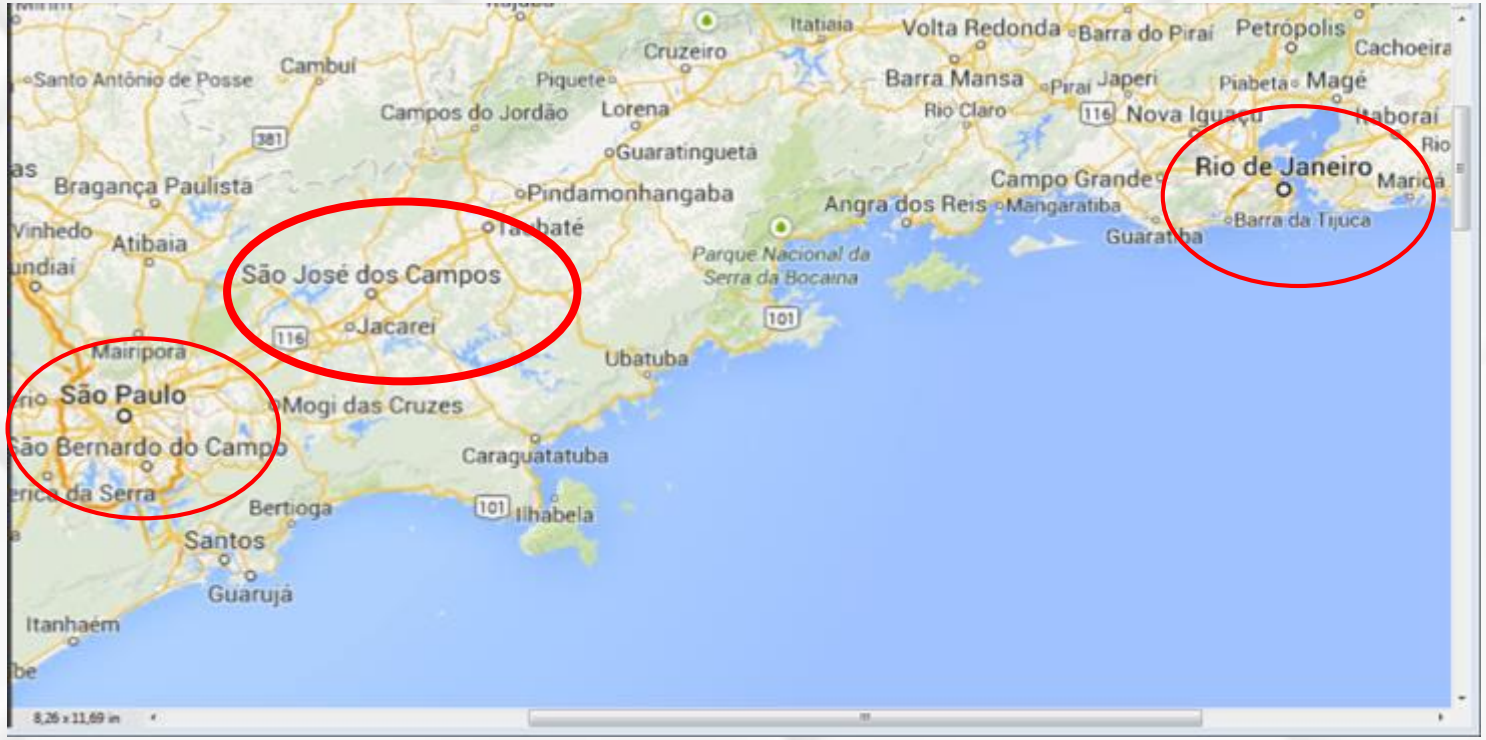
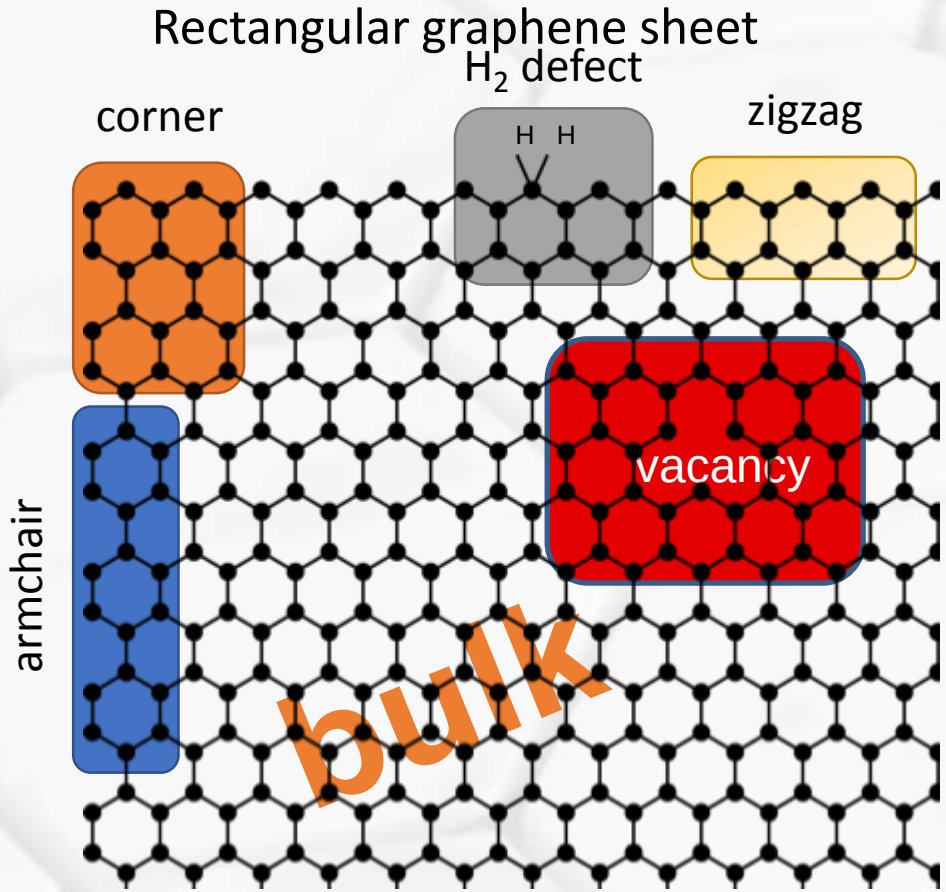


Technological Institute of Aeronautics (ITA) - 1950

Motivation: Graphene Properties, Polyaromatic Hydrocarbons (PAH), chemical reactivity, excited states

design new material



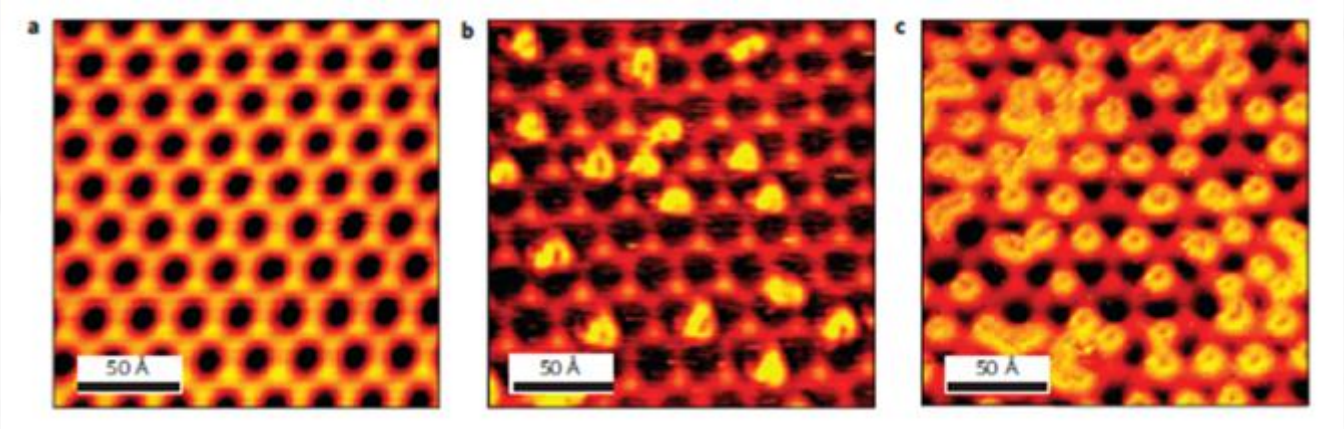
Properties:

- 100 times stronger than the strongest steel
- Conducts heat and electricity efficiently
- Zero-gap semiconductor

Applications:
chemical sensors, organic semiconductors, energy storage devices, spintronics and nonlinear optics

K. S. Novoselov, A. K. Geim, et al., Science, **306** (2004) 666

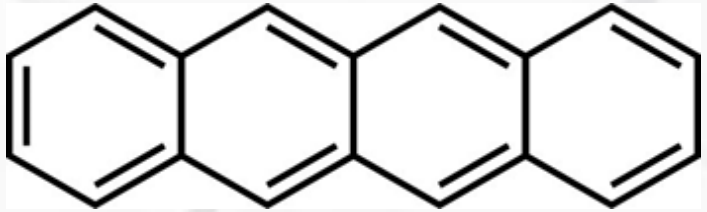
Motivation: Chemical reactivity, Radical Character



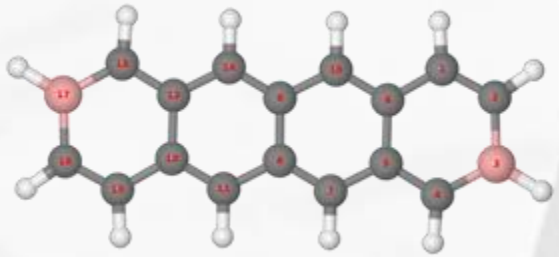
"Bandgap opening in graphene induced by patterned hydrogen adsorption"

R. Balog, et al. Nat. Mater. **9** (2010) 315

Polycyclic Aromatic Hydrocarbons (PAH)



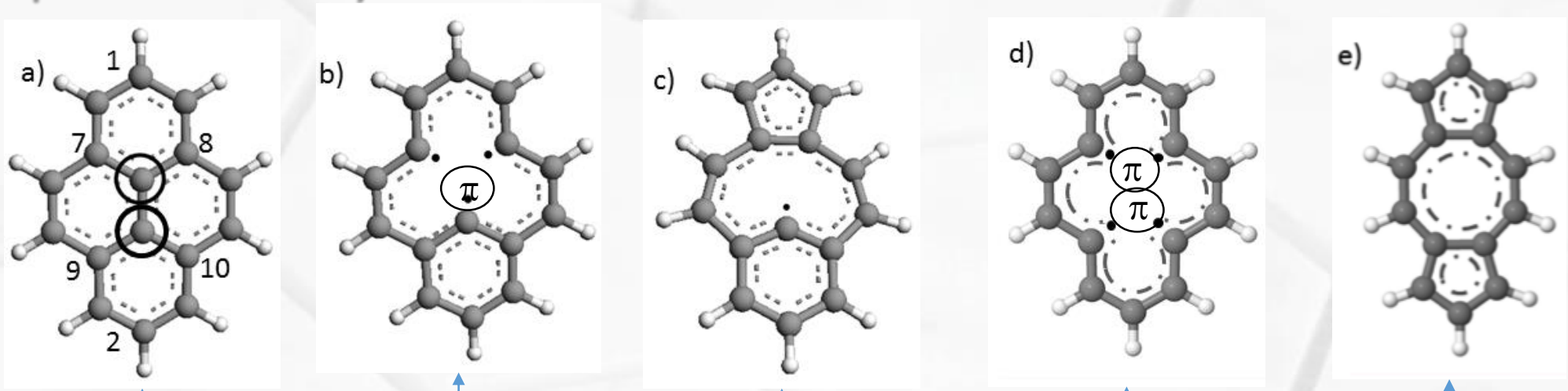
Polyacenes



chemical doping

Pyrene

First Collaboration work (2013-2014): Single and Double Vacancies Defects in Graphene: Pyrene model



C_7-C_8=2.47 Å

a) original unperturbed. DFT/B3LYP/6-31G**

c) 1C-relaxed. CASSCF (6,6)

e) 2-C relaxed. CASSCF (8,8)

b) unrelaxed 1C-vacancy

d) unrelaxed 2C-vacancies

F. B. C. Machado, A. J. A. Aquino and H. Lischka, ChemPhysChem **15** (2014) 3334

F. B. C. Machado, A. J. A. Aquino and H. Lischka, PCCP **17** (2015) 12778

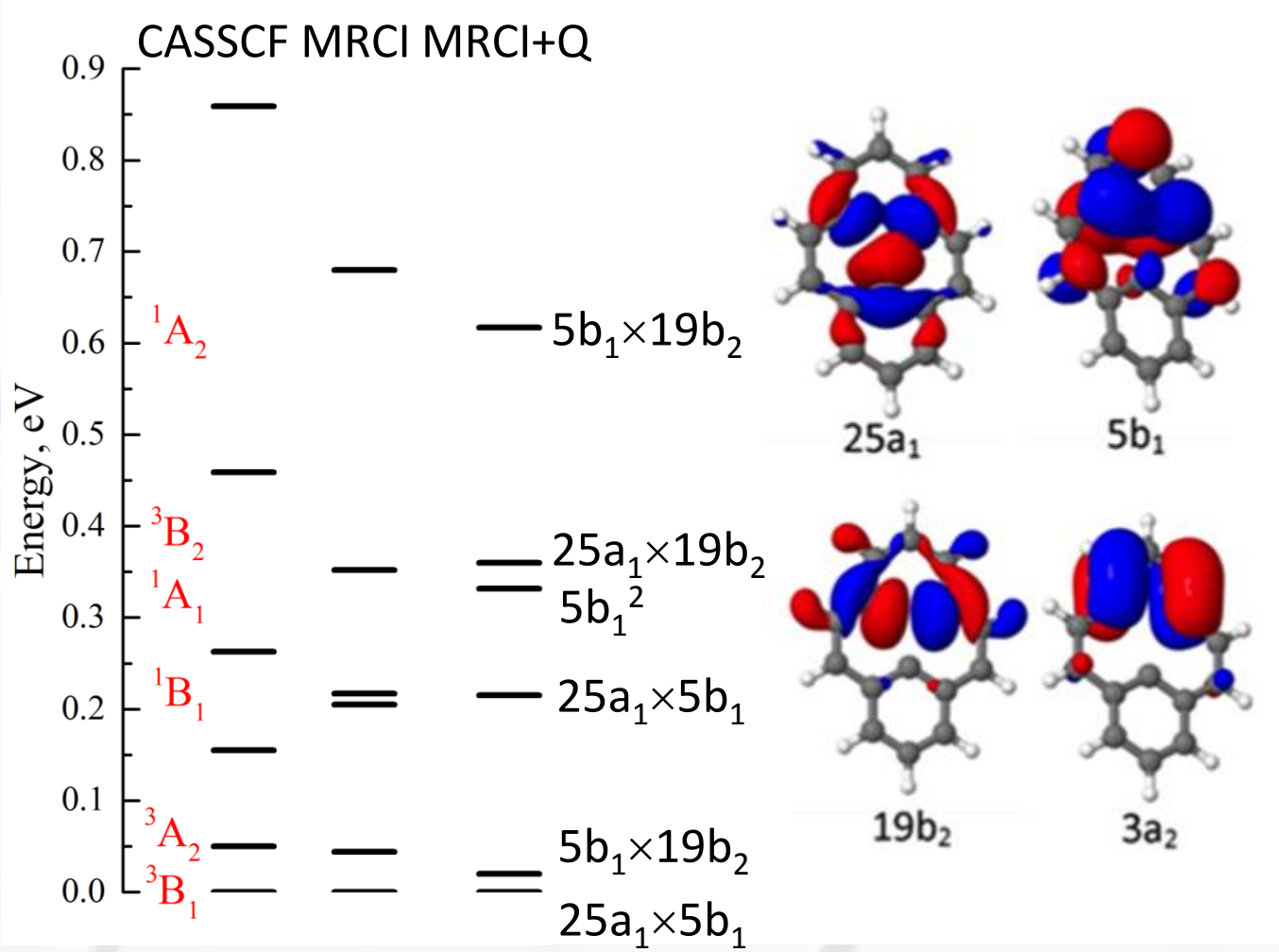
Electronic States

- 1C-Vacancy- Unrelaxed

The $25a_1$ and $19b_2$ orbitals represent approximately the degenerate set of e' orbitals.

They appear in $^3B_1$ and $^3A_2$ combined with $5b_1$ orbital.

Closed shell part: $24a_1^2 4b_1^2 18b_2^2 2a_2^2$



F. B. C. Machado, A. J. A. Aquino and H. Lischka, ChemPhysChem **15** (2014) 3334

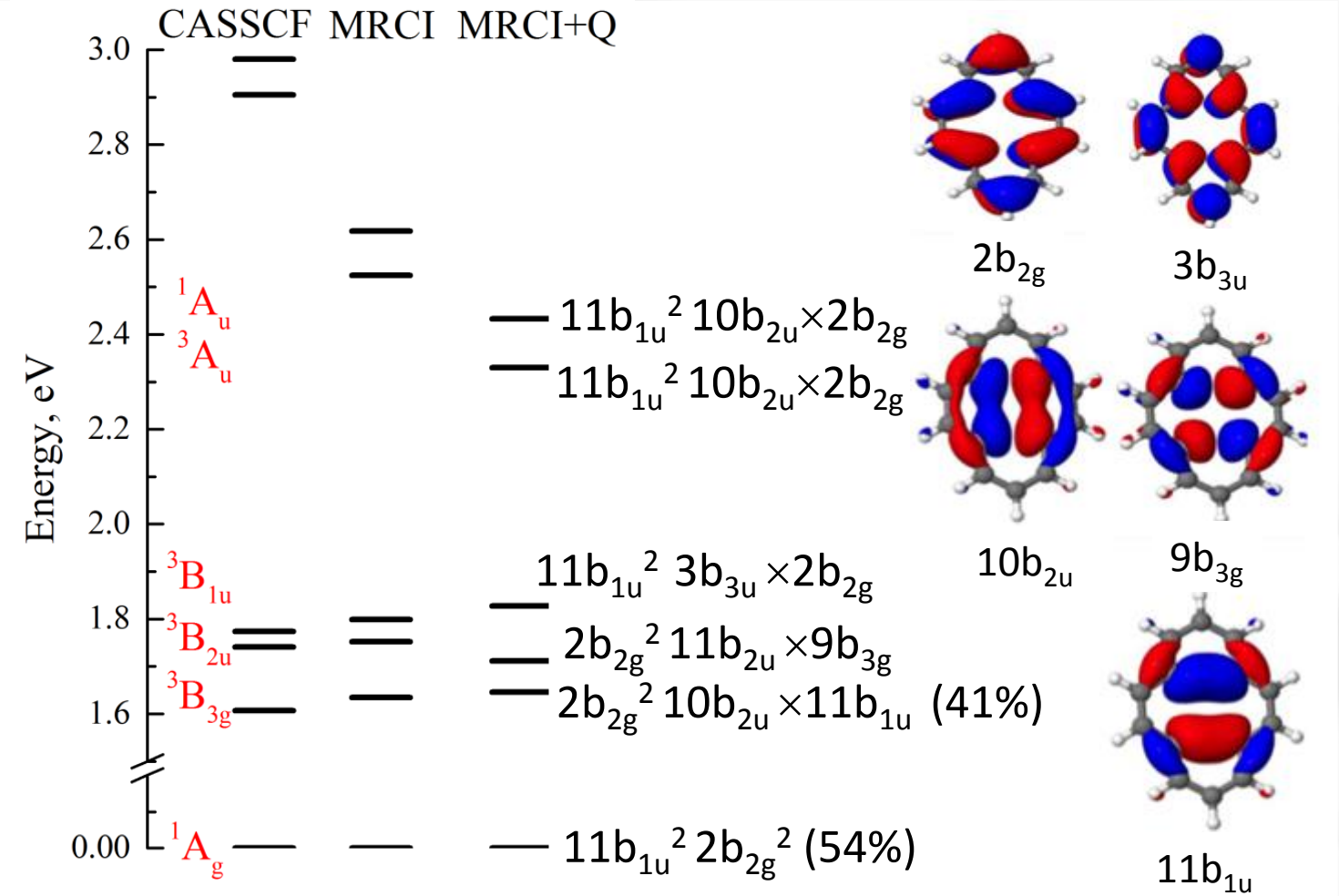
2C-Vacancy- Unrelaxed

^1A_g is the ground state first five excited states $^3B_{3g}$, $^3B_{2u}$, $^3B_{1u}$, ^3A_u, ^1A_u lie above 1.6 eV.

Strong multireferencial Character

The $11b_{1u}$ is σ bonding, the $10b_{2u}$ and $9b_{3g}$ are σ* antibonding, the $2b_{2g}$ and $3b_{3u}$ are π orbitals bonding.

$^3B_{3g}$, $^3B_{2u}$, arise from the σ-σ*
^3A_u, ^1A_u from π-σ*
$^3B_{1u}$ from π-π excitation.



Closed shell part: $12a_g^2\,2b_{3u}^2\,9b_{2u}^2\,2b_{1g}^2\,10b_{1u}^2\,1b_{2g}^2\,8b_{3g}^2\,1a_u^2$

F. B. C. Machado, A. J. A. Aquino and H. Lischka, PCCP **17** (2015) 12778

Proposal Goals: Sprint (2015-2017)

- Description of the *electronic structure* excited states of the vacancy defects using extended models
- Chemical reactivity
- Stacked dimers of polyaromatic hydrocarbons as models for graphene sheet interactions
- Acenes Excited States
- Chemical doping

METHODS:

- **Electronic states:**
- *Ab initio* methods as benchmark: CASSCF/MRCI
- Density functional theory for larger molecular systems

Polyradical character:

Effective unpaired electron densities and total number of effectively unpaired electrons (N_U)[1,2]:

$$N_U = \sum_{i=1}^{M} {n_i}^2 (2 - n_i)^2$$

MR calculations : COLUMBUS program

CASSCF optimizations: **DL-FIND** interfaced to COLUMBUS

DFT: TURBOMOLE

[1] V. N. Staroverov, E. R. Davidson, Chem. Phys. Lett. 2000, 330, 161 –168.

[2] M. Head-Gordon, Chem. Phys. Lett. 2003, 372, 508–511.

Progress Report

Exchange visits:

F. B. C. Machado: two visits to TTU in 2016 : February 21 – March 04, 2016 and August 31 – September 09

J. A. Aquino: one visit to ITA : August 12-19, 2016

H. Lischka: two visits to ITA : April 22-24, 2015, August 12-19, 2016

Publications:

- N. J. Silva, F. B. C. Machado, H. Lischka, A. J. A. Aquino, π-π Stacking between Polyaromatic Hydrocarbon Sheets beyond Dispersion Interactions, PhysChemChemPhys **18** (2016) 22300-22310
- R. Nieman, A. Das, A. A. J. Aquino, R. G. Amorim, F. B. C. Machado, H. Lischka, Single and Double Carbon Vacancies in Pyrene as First Models for Graphene Defects: A Survey of the Chemical Reactivity toward Hydrogen, Chem. Phys. **482** (2017) 346-354
- M. Pinheiro Jr., L. F. A. Ferrão, F. Bettanin, A. J. A. Aquino, F. B. C. Machado, H. Lischka, How to tune efficiently the biradicaloid nature of acenes by chemical doping with boron and nitrogen, PhysChemChemPhys **19** (2017) 19225-19233
- A. D. Powell, N. S. Dattani, R. F. K. Spada, F. B. C. Machado, H. Lischka, R. Dawes, Investigation of the ozone formation reaction pathway: Comparisons of Full Configuration Interaction Quantum Monte Carlo and Fixed-Node Diffusion Monte Carlo with contracted and uncontracted MRCI, J. Chem. Phys. **147**, (2017) 094306
- F. Bettanin, L. F. A. Ferrão, M. Pinheiro Jr, A. J. A. Aquino, H. Lischka, F. B. C. Machado, D. Nachtigallova, The singlet L_a and L_b bands for N-acenes (N = 2 to 7): An CASSCF/CASPT2 study, J. Chem. Theory Comput. **13** (2017) 4297- 4306

Progress Report

Publication in preparation:

- D. V. V. Cardoso, M. Pinheiro Jr, A. J. A. Aquino, F. B. C. Machado, H. Lischka, The Characterization of Electronic Defect States of Single and Double Carbon Vacancies in Graphene Sheets Using Molecular Density Functional Theory
- R. G. Amorim, R. Nieman, A. Das, A. A. J. Aquino, F. B. C. Machado H. Lischka, Graphene reactivity investigation using pyrene and extended pyrene model
- A. Das, M. Pinheiro Jr., F. B. C. Machado, A. J. A. Aquino, H. Lischka, Efficient Modulation of the Singlet Open Shell Character of Heptazethrene by Nitrogen Doping
- M. Pinheiro Jr, A. Das, A. J. A. Aquino, F. B. C. Machado, H. Lischka, The Variation of Singlet Polyradical Character in Polyacenes Induced by Nitrogen Doping Revealed by means of Singlet/Triplet Splittings

Workshop/School:

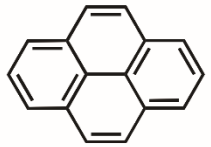
- "3a Escola de Química Computacional – Theory of new materials at atomistic level: Graphene, Graphene Defects and π-Conjugated Polyradical Systems", Hans Lischka, Rodrigo Amorim, Francisco B. C. Machado (scientific coordinators), Nelson H. Morgon, Ricardo Vessecchi, (coordinators), **Sergio E. Galembeck** (general coordinator), Ribeirao Preto, Brazil, December 11 – 14, 2017, project accepted by the University of Sao Paulo and by **FAPESP**

15 oral presentations

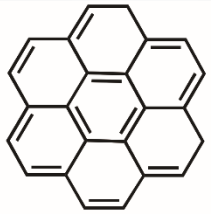
Calculation of Stacking Energies

Stacked dimers of polyaromatic hydrocarbons as models for graphene sheet interactions

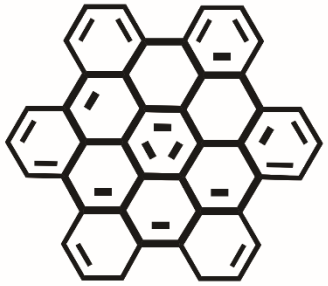
High-level *Ab Initio* Methods vs. DFT



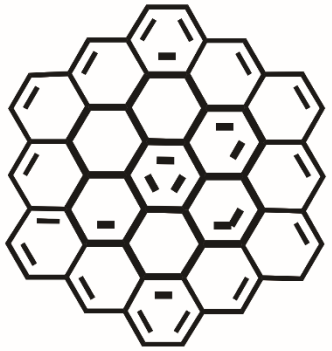
pyrene



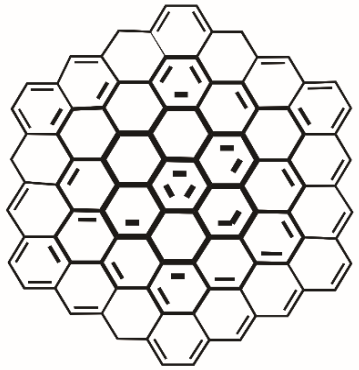
coronene



hexabenzocoronene



coronene circum-1



coronene circum-2

N. J. Silva, TTU

DFT does not include dispersion interaction, empirical corrections are added on top

Ab initio methods include all interaction terms correctly but are computationally much more expensive

Methods used: CCSD(T)-F12, CCSD(T), **SOS-MP2**, MP2, DFT/PBE-D3, B97-D2/def2-TZVP

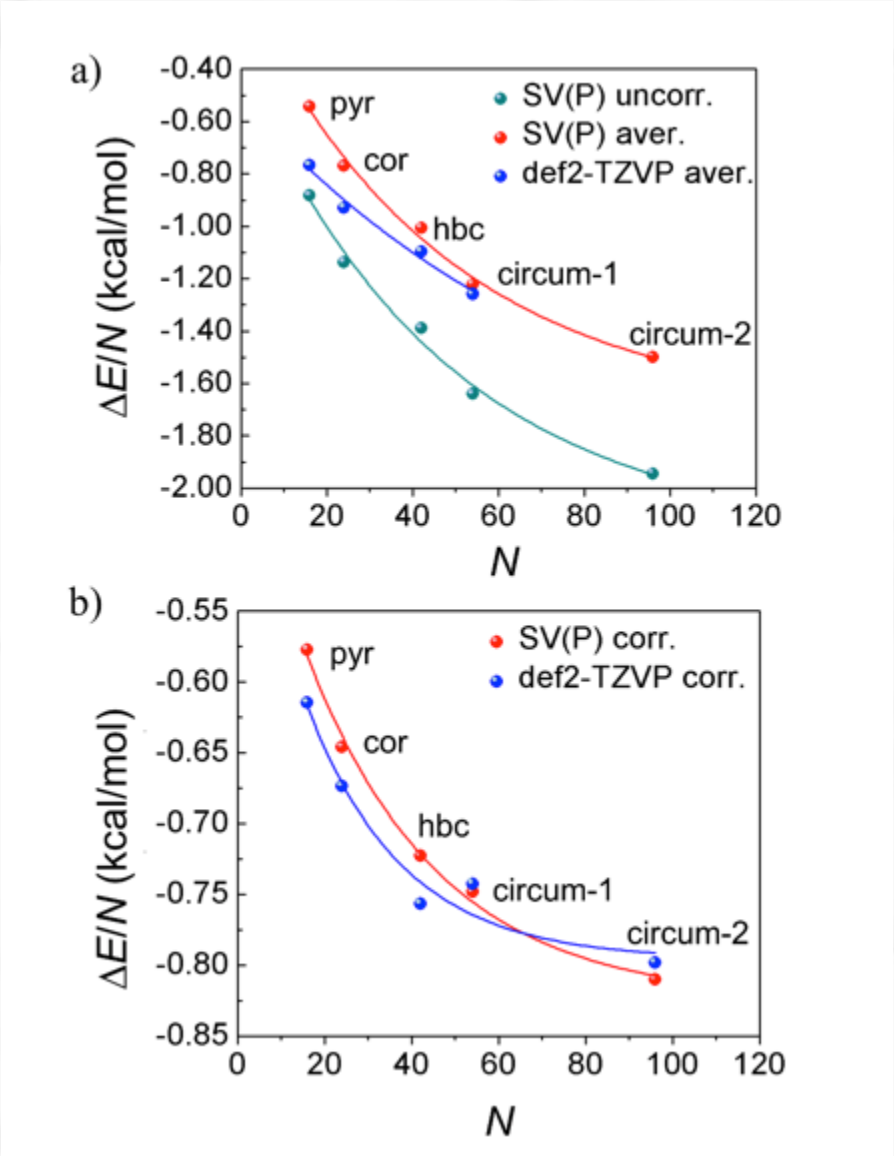
N. J. Silva, F. B. C. Machado, H. Lischka and A. J. A. Aquino, PhysChemChemPhys **18** (2016) 22300

Calculation of Stacking Energies

Ab initio/DFT comparisons

SOS-MP2

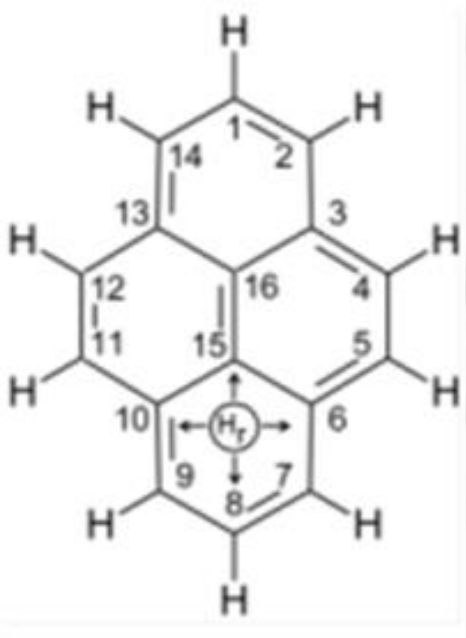
DFT/PBE

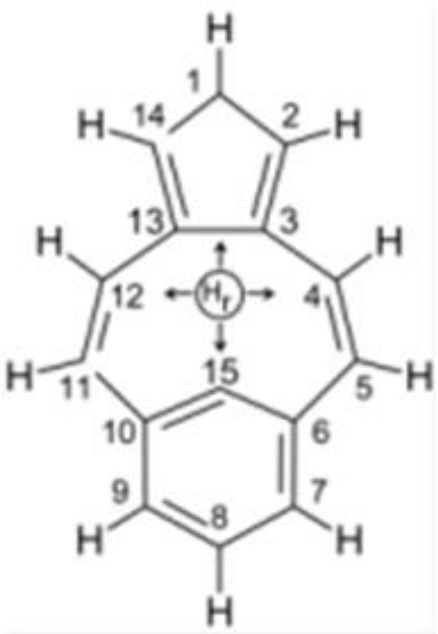


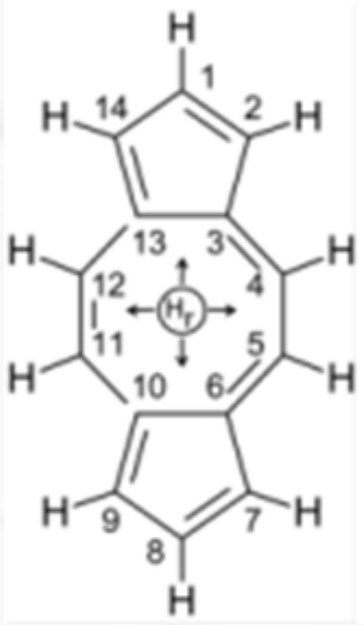
N. J. Silva, F. B. C. Machado, H. Lischka and A. J. A. Aquino, PhysChemChemPhys **18** (2016) 22300

Reactivity toward Hydrogen

formation of sp^3 defects and chemical reactions







R. Nieman, TTU

Planar pyrene relaxed structures :
The potential energy scan (PES) : H_r fixed at 1.0 Å from the plane move around a grid with at an increment of 0.3 Å . SA4-CASSCF (5,5) /6-31G*

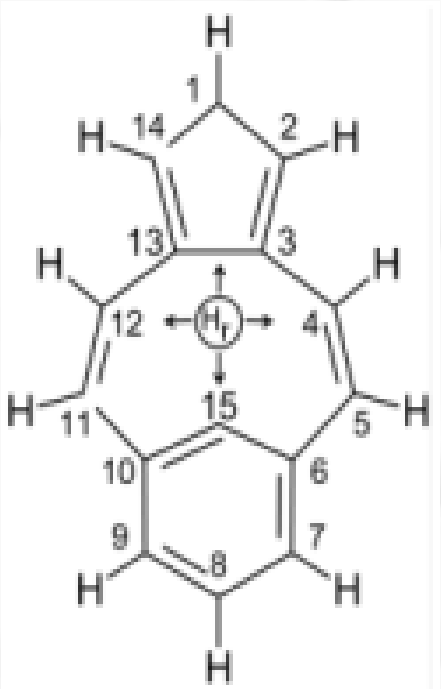
Geometry optimizations: carbons connected to hydrogen atoms at the periphery were always frozen, other atoms relaxed.

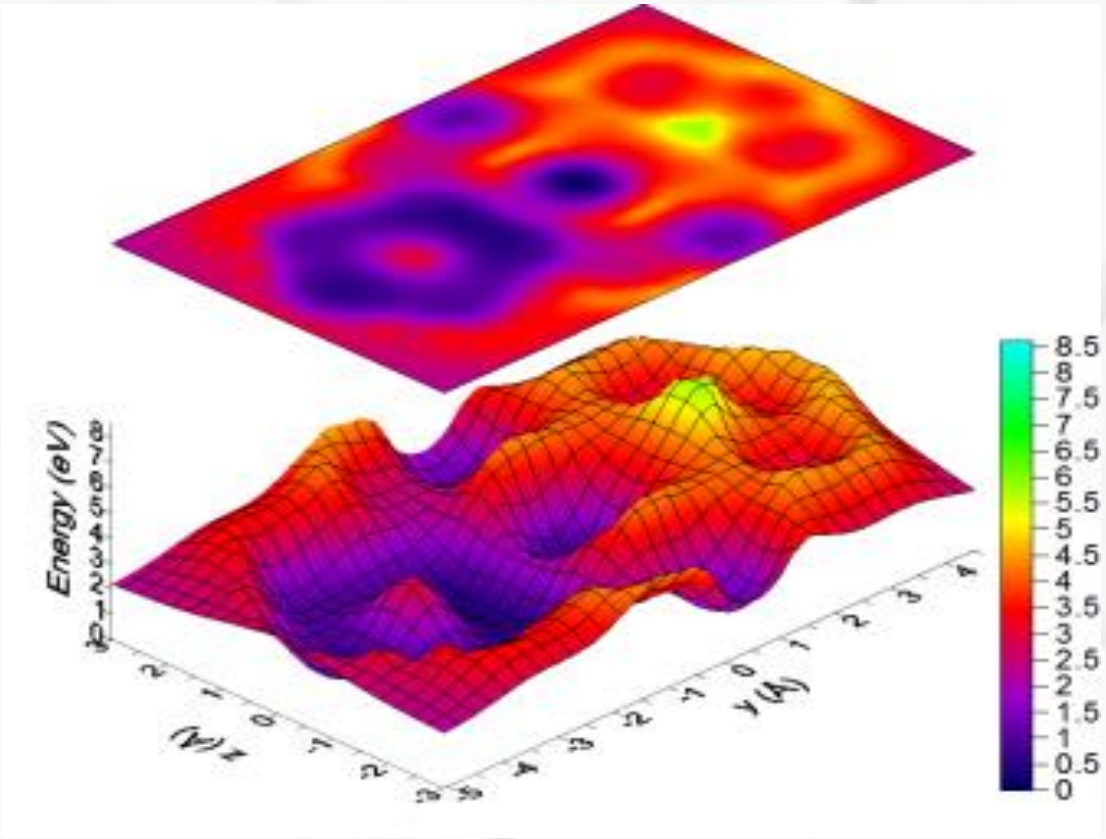
R. Nieman, A. Das, A. A. J. Aquino, R. G. Amorim, F. B. C. Machado, H. Lischka. Chem. Phys. **482** (2017) 346

Results: reactivity toward hydrogen

is a test radical, e.g. OH, H ⇒ formation of sp^3 defects and chemical reactions

Pyrene-1C+H

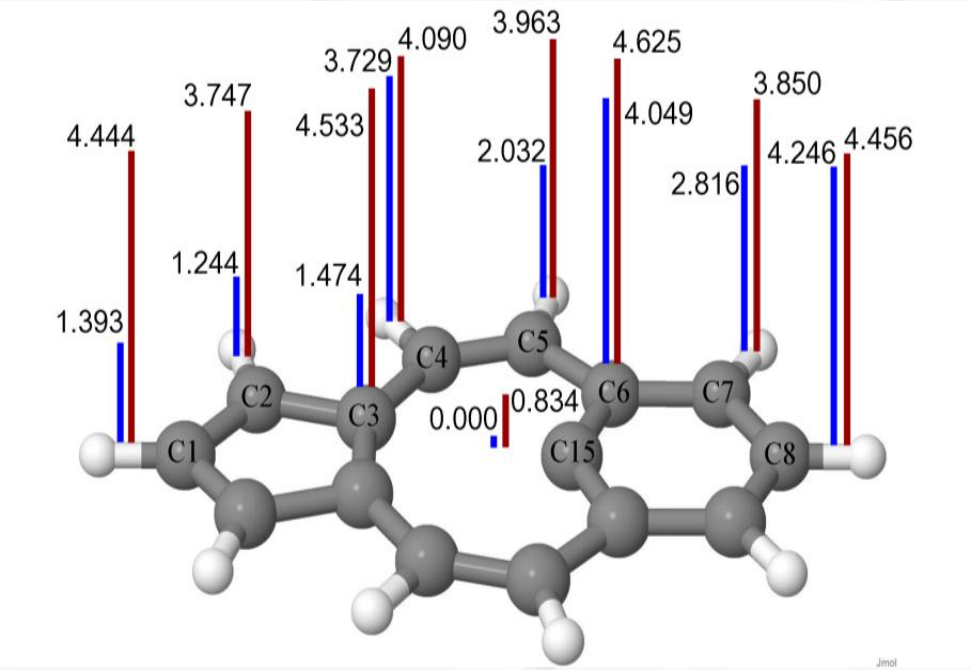




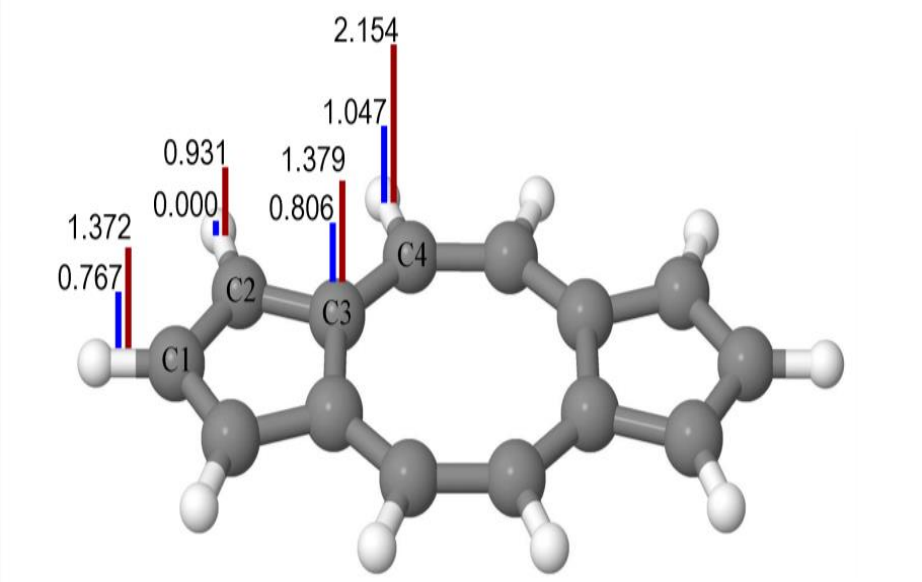
SA4-CASSCF(5,5)/6-31G* - Electronic ground state (1^2A)

R. Nieman, A. Das, A. A. J. Aquino, R. G. Amorim, F. B. C. Machado, H. Lischka. Chem. Phys. **482** (2017) 346

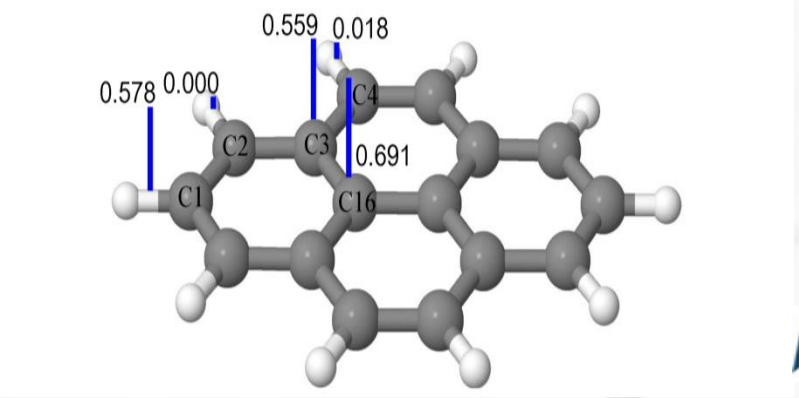
Pyrene-1C +H: Energy Minima (eV)



Pyrene-2C +H: Energy Minima (eV)



Pyrene+H: Energy Minima (eV)

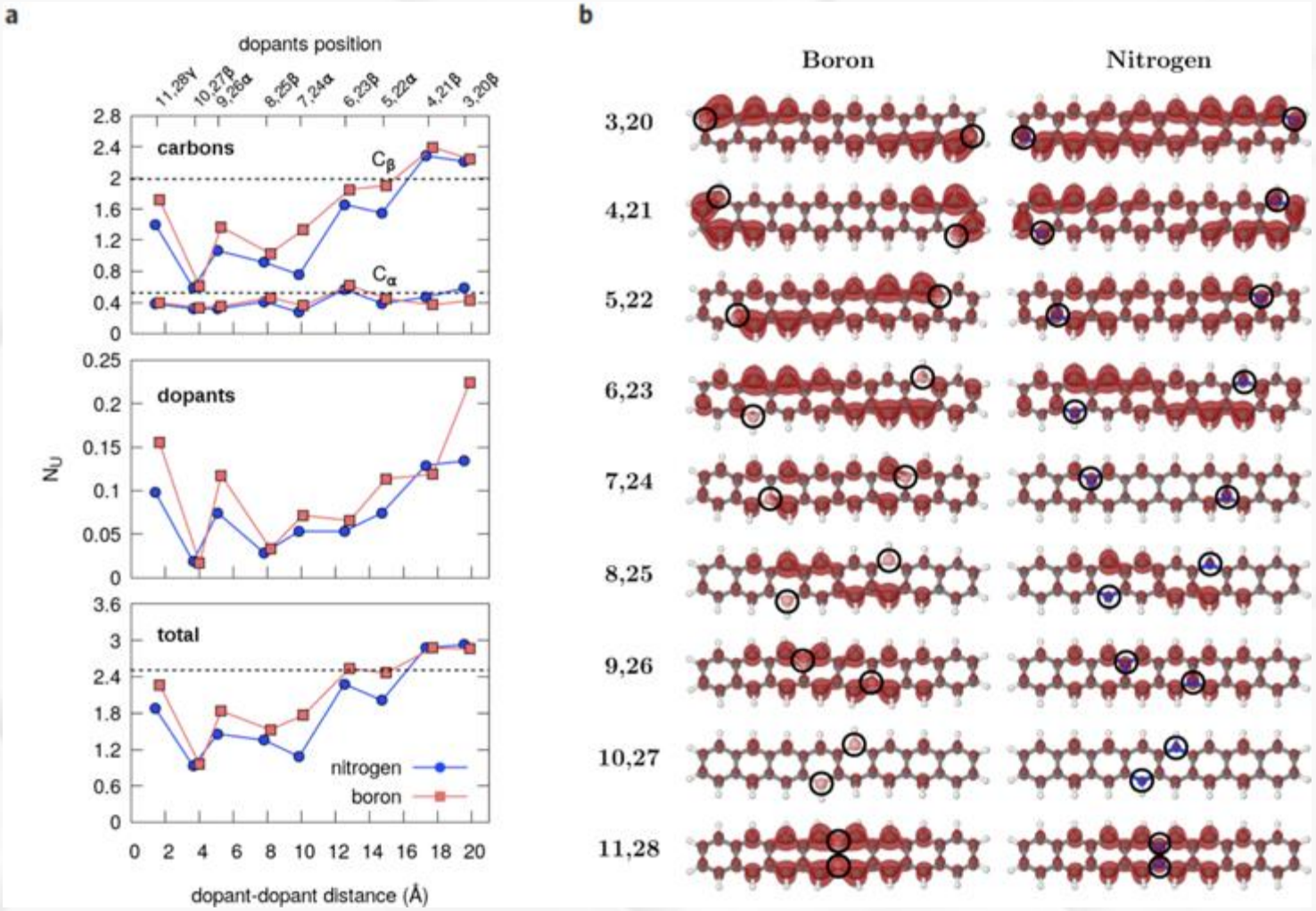


Blue: Ground state, red: first excited state
MRCI+Q (5,5)/6-31G*

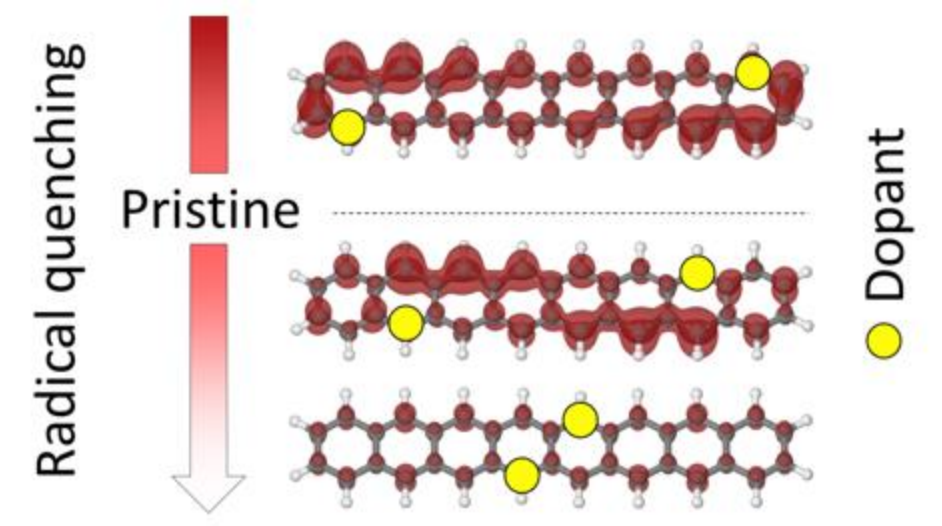
R. Nieman, A. Das, A. A. J. Aquino, R. G. Amorim, F. B. C. Machado, H. Lischka. Chem. Phys. **482** (2017) 346

How to tune efficiently the biradicaloid nature of acenes by chemical doping with boron and nitrogen

Chemical doping ➞ substitution of two carbons atoms by Boron (B) or Nitrogen (N)

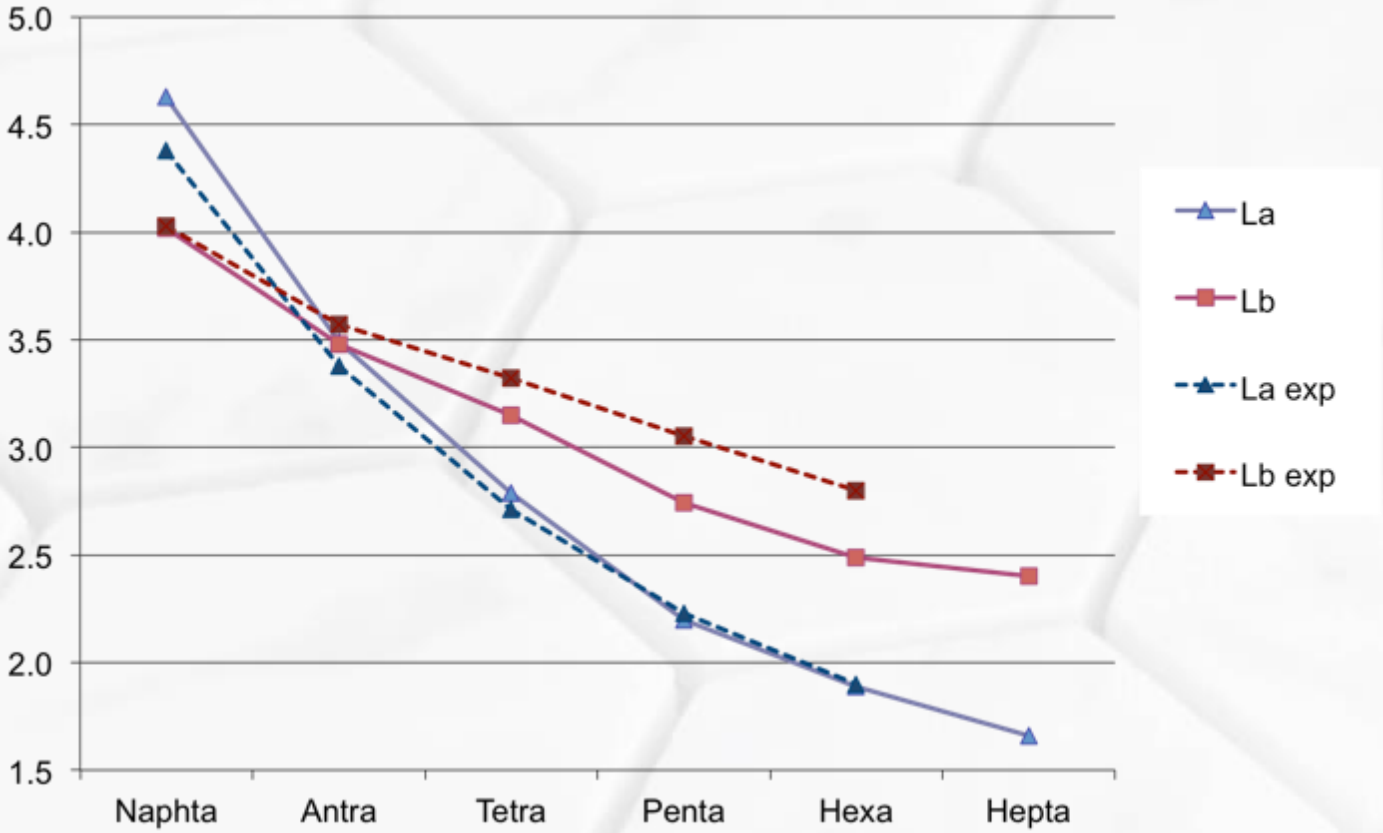


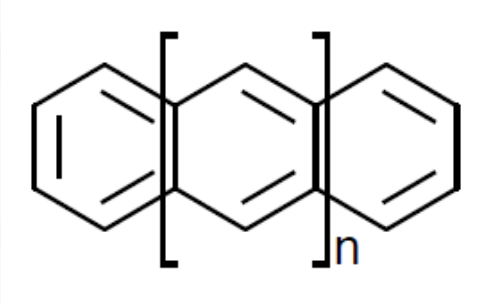
M. Pinheiro Jr., ITA



M. Pinheiro Jr., L. F. A. Ferrão, F. Bettanin, A. J. A. Aquino, F. B. C. Machado, H. Lischka, PhysChemChemPhys **19** (2017) 19225

Acenes Excited States: Absorption Spectra: L_a and L_b bands





n=0 to n=5

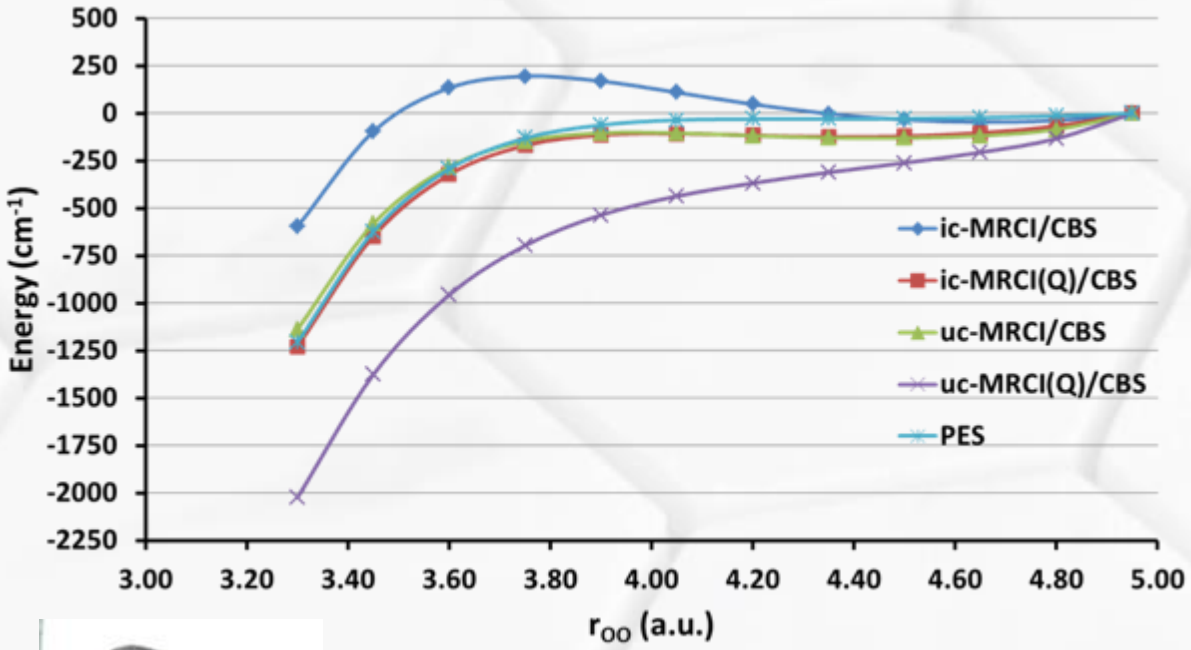
F. Bettanin, ITA

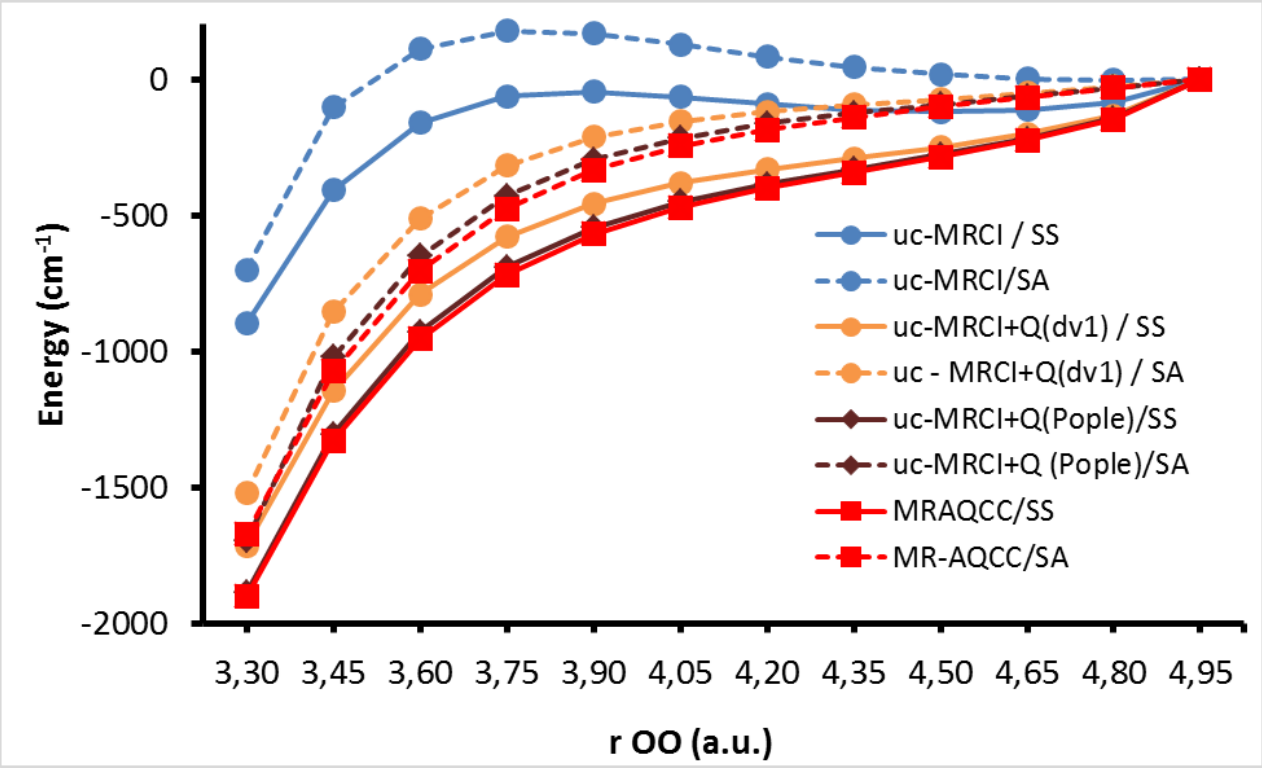
Methodology: CASPT2
Active space: CAS(14,14)
Frozen orbitals: 1s

L_a band: HOMO -> LUMO transition; ionic; dinamic correlation dependence
L_b band: HOMO-1 -> LUMO and HOMO -> LUMO+1 transitions; covalent character; static correlation dependence

F. Bettanin, L. F. A. Ferrão, M. Pinheiro Jr., A. J. A. Aquino, H. Lischka, F. B. C. Machado, D. Nachtigallova, J. Chem. Theory Comput., **13** (2017) 4297

Comparison of MRCI calculation on ozone dissociation



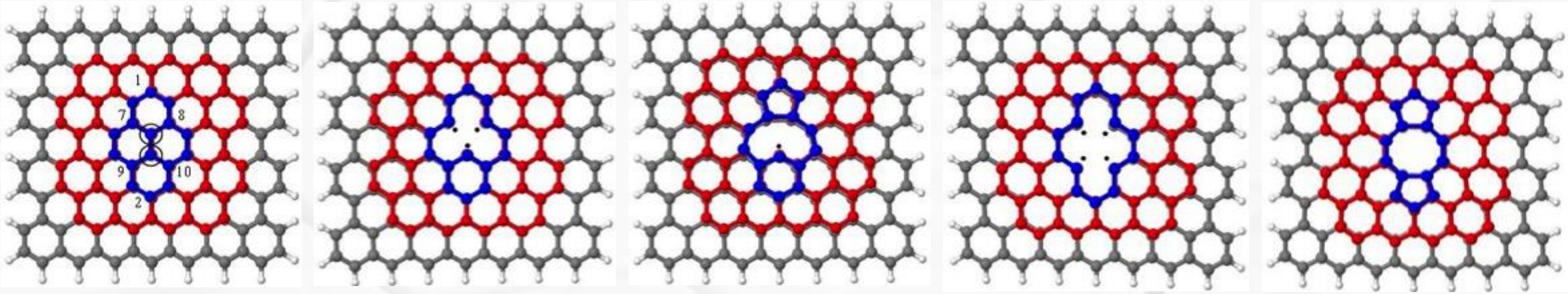


R. F. K. Spada, ITA

A. D. Powell, N. S. Dattani, R. F. K. Spada, F. B. C. Machado, H. Lischka, R. Dawes, *J.* Chem. Phys. **147** (2017) 094306

In Progress: Vacancies: Extended Systems

a) b) c) d) e)



a) original unperturbed structures with numbering of selected carbon atoms, the circles indicate the carbon atoms to be removed, pyrene (blue), extended pyrene (red) and 7a, 7z-periacene (gray).

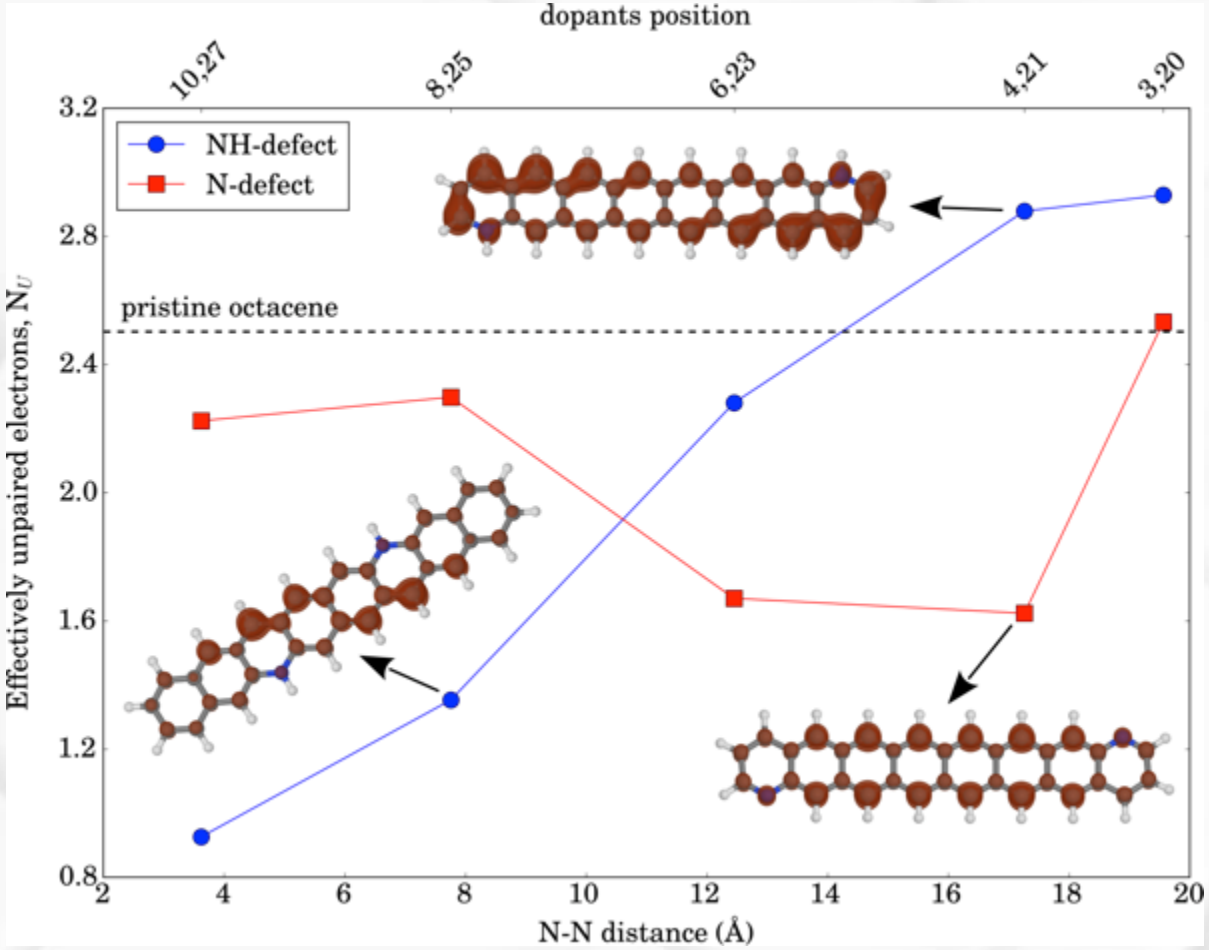
b) structures-1C-unrel,
c) structures-1C-relaxed,
d) structures-2C-unrel,
e) structures-2C-relaxed.

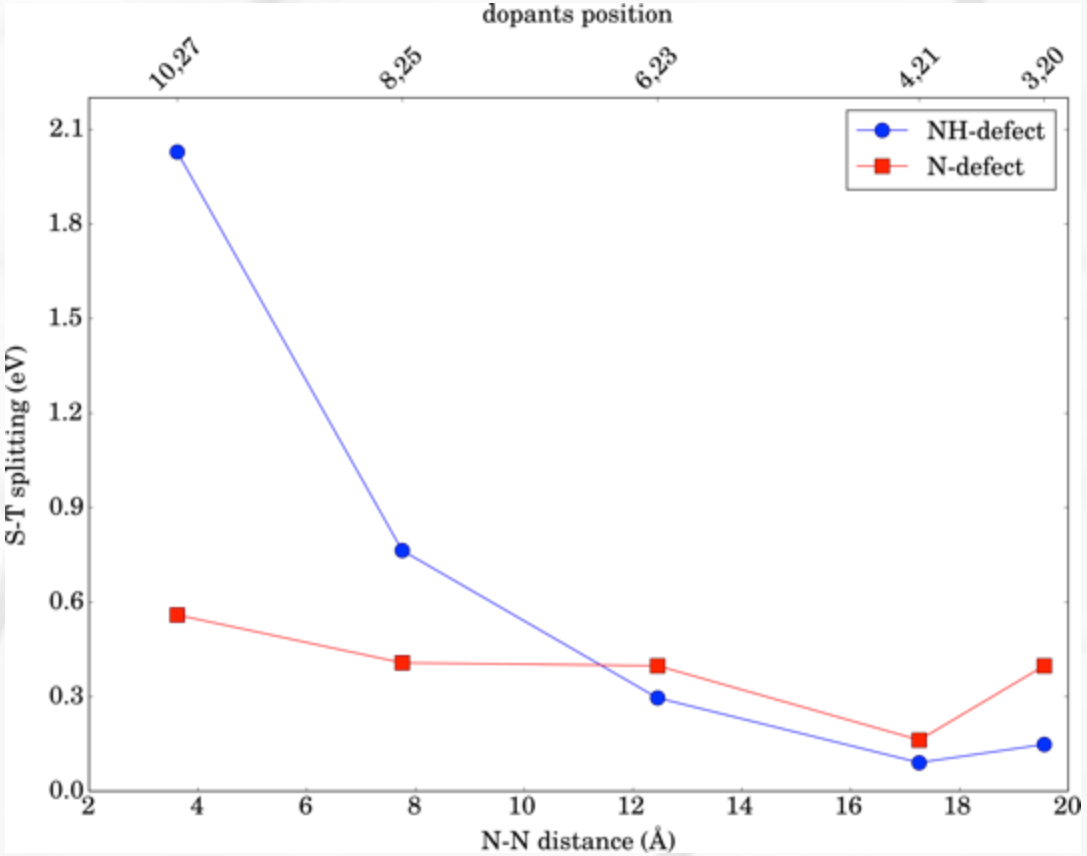
D. V. V. Cardoso, ITA

D. V. V. Cardoso, M. Pinheiro Jr., A. A. J. Aquino, F. B. C. Machado, H. Lischka. *To be submitted.*

Acenes with N substitution: pyridinic-like vs. pyrrolic-like

M. Pinheiro Jr., ITA





M. Pinheiro Jr, A. Das, A. J. A. Aquino, F. B. C. Machado, H. Lischka (2017). In preparation

Acknowledgment

Prof. Hans Lischka

Prof. Adelia Aquino

Prof. Bill Hase

A.Das, TTU

R. Amorim, ITA

Thank you