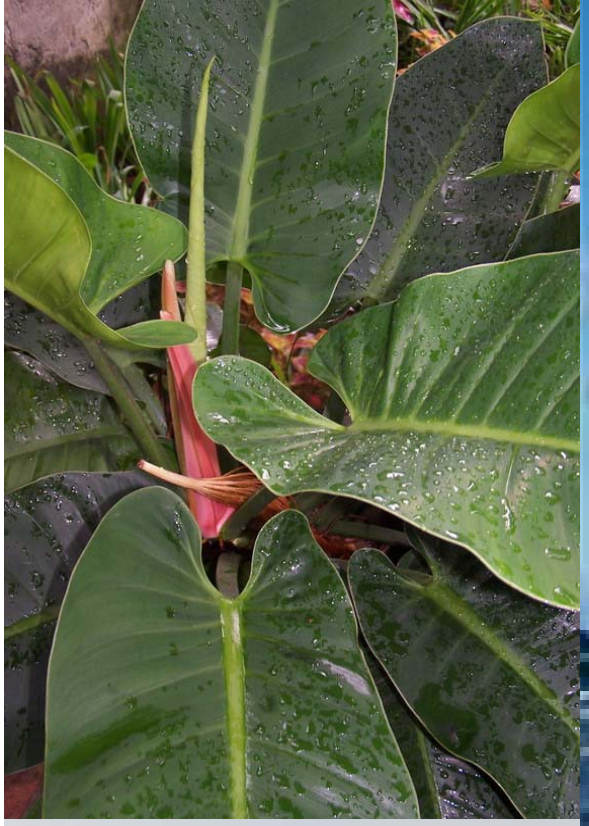

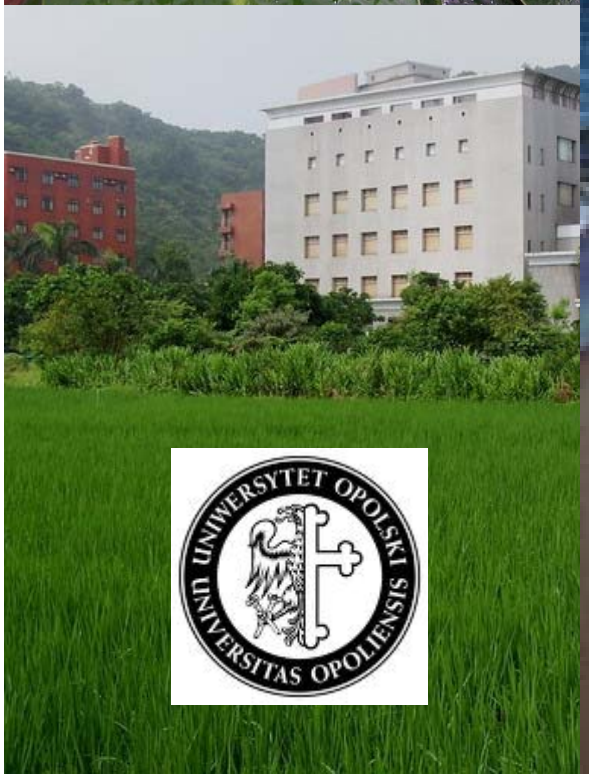

Molecular modeling of graphene. N-doping of basic structural units

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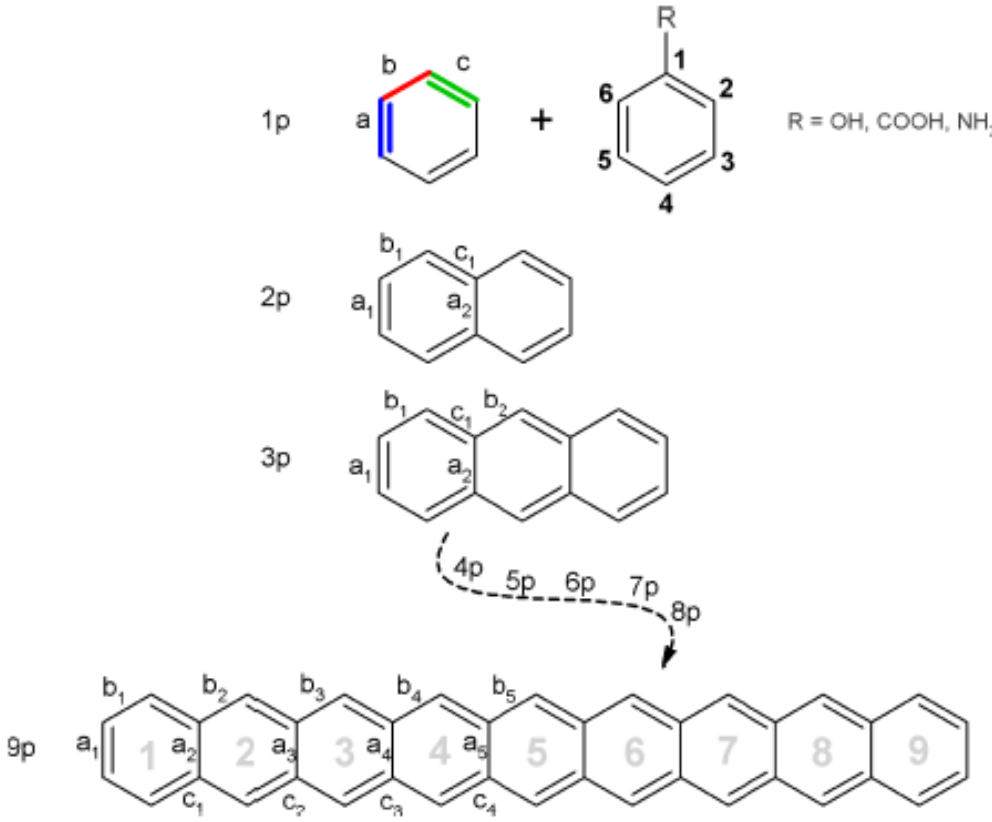
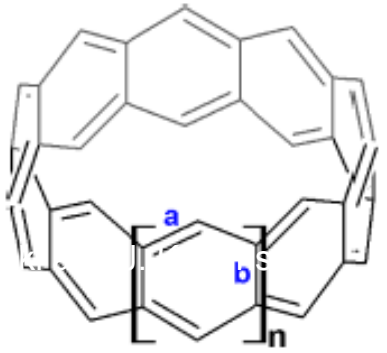
WPROWADZENIE

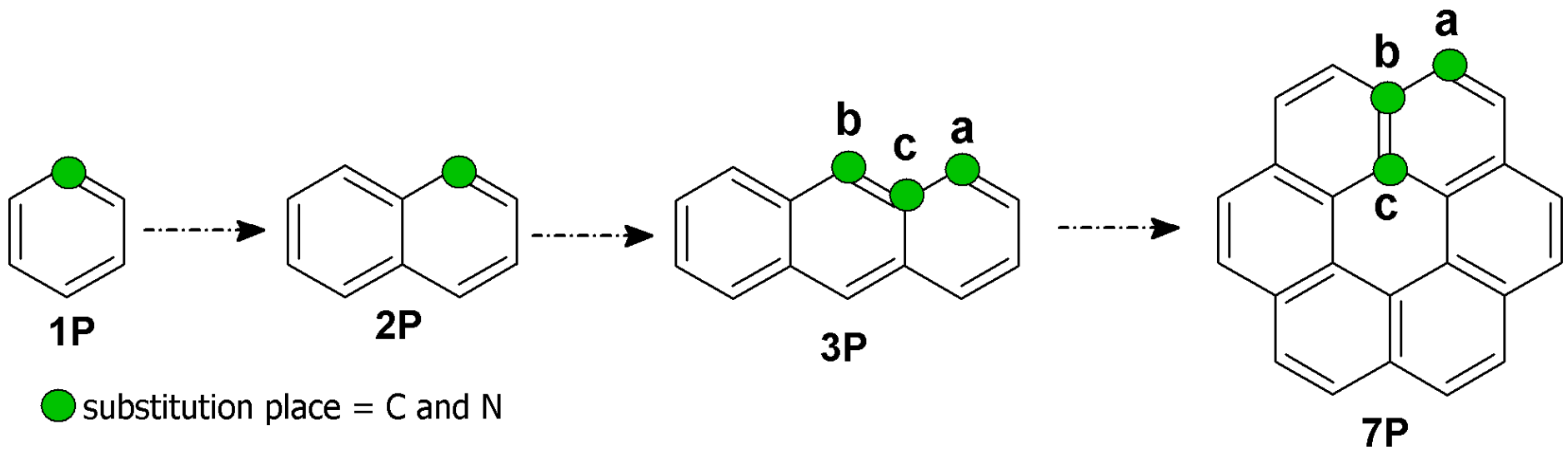
1. Wstęp
2. Grafen dopowany
3. Szczegóły
5. Podziękowania

Scheme 1. Bond Labeling in Linearly Conjugated Planar (p) Benzene Rings (acenes, n = 1–9)



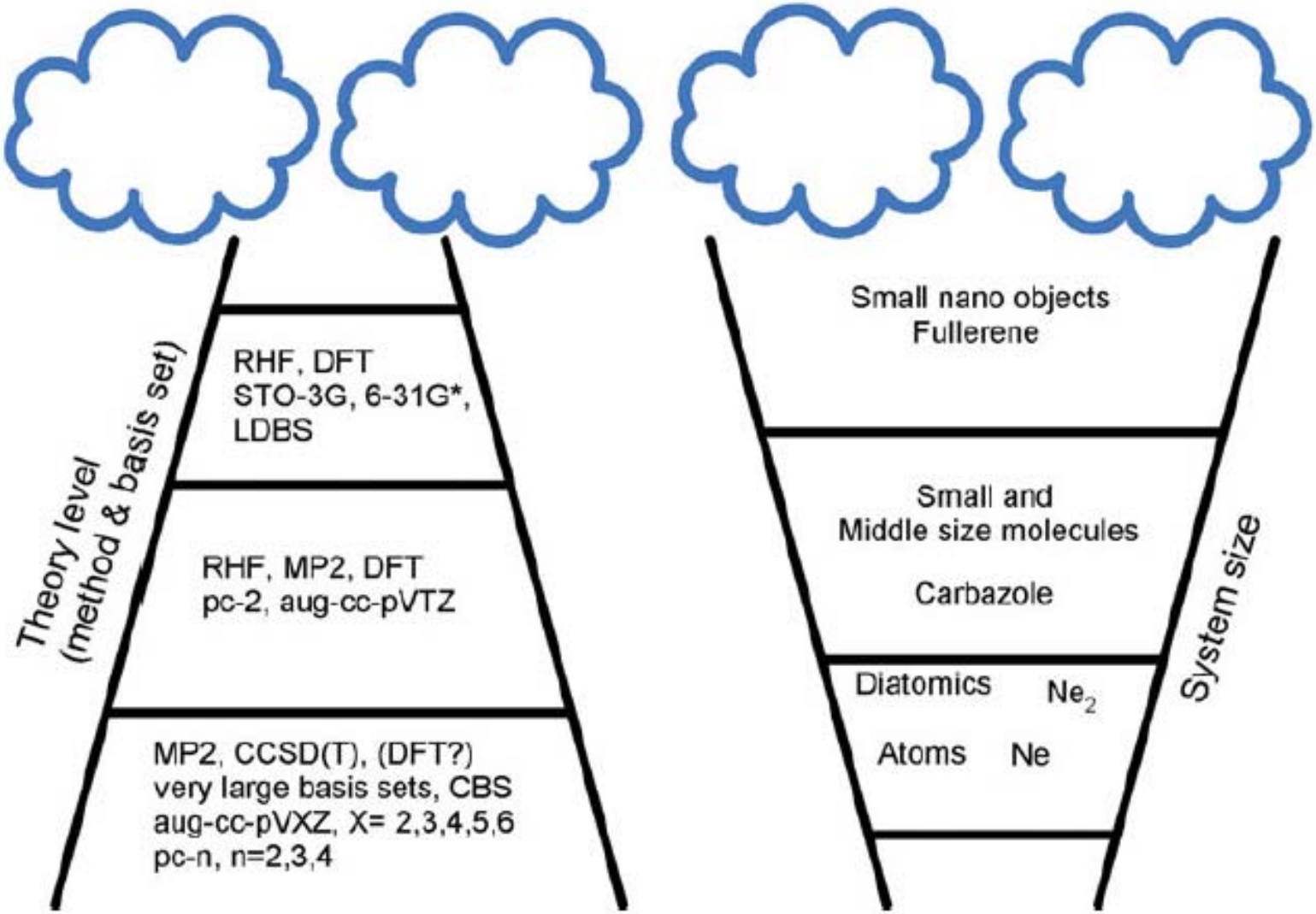
Scheme 2. Bond Labeling in Molecular "Belt" Systems (Cyclacenes, where n = 4–8)





UB3LYP/6-311++G** GEOMETRY, GIAO NMR

HOMO LUMO



Scheme 1. 'Jacob's Ladder' explaining a compromise between system size and theory level.

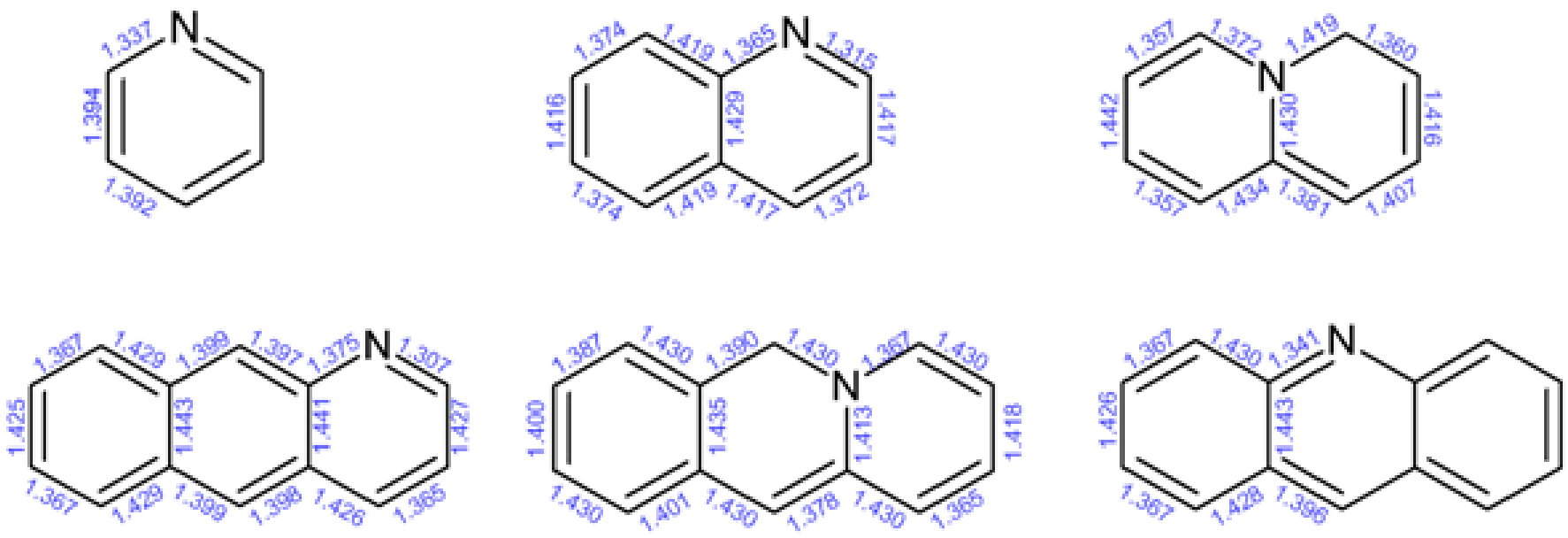


Fig. S1. UB3LYP/6-311++G** optimized CC and CN bond lengths in the studied molecules 1P – 3P

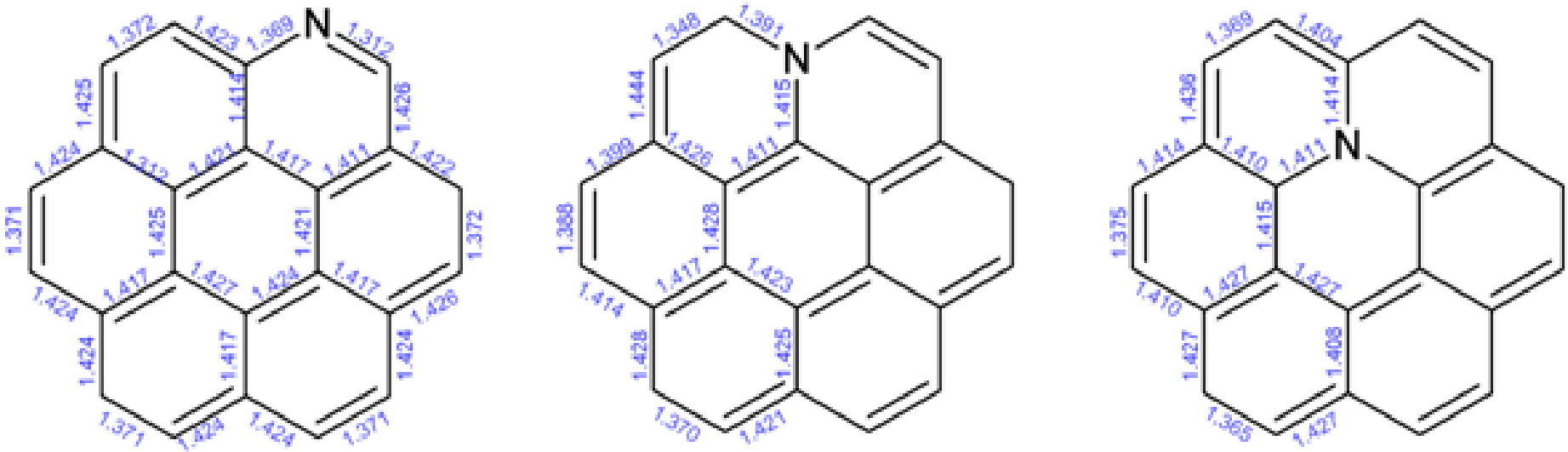


Fig. S2. UB3LYP/6-311++G** optimized CC and CN bond lengths in the studied molecules 7P

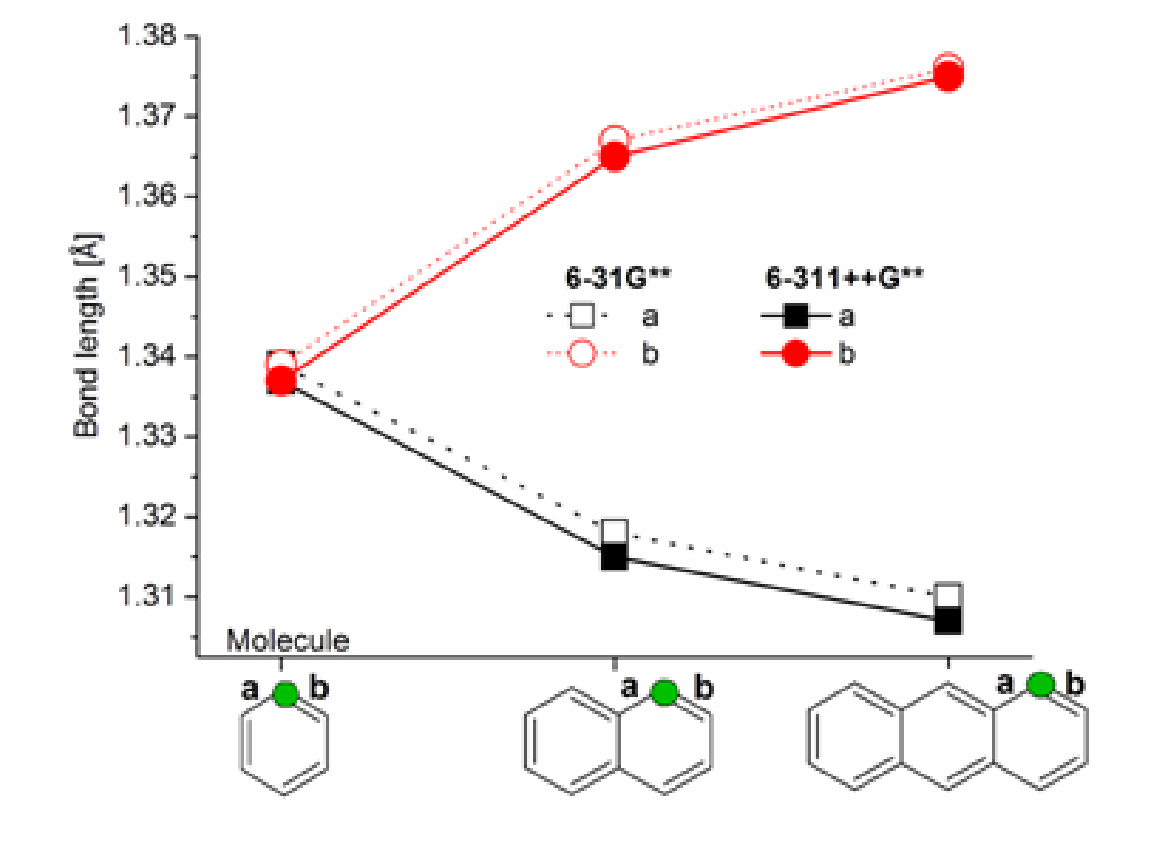


Figure 1. Change of two C-N bonds in pyridine ring upon addition of one and two benzene rings. The results are calculated with UB3LYP density functional combined with 6-31G** and 6-311++G** basis sets

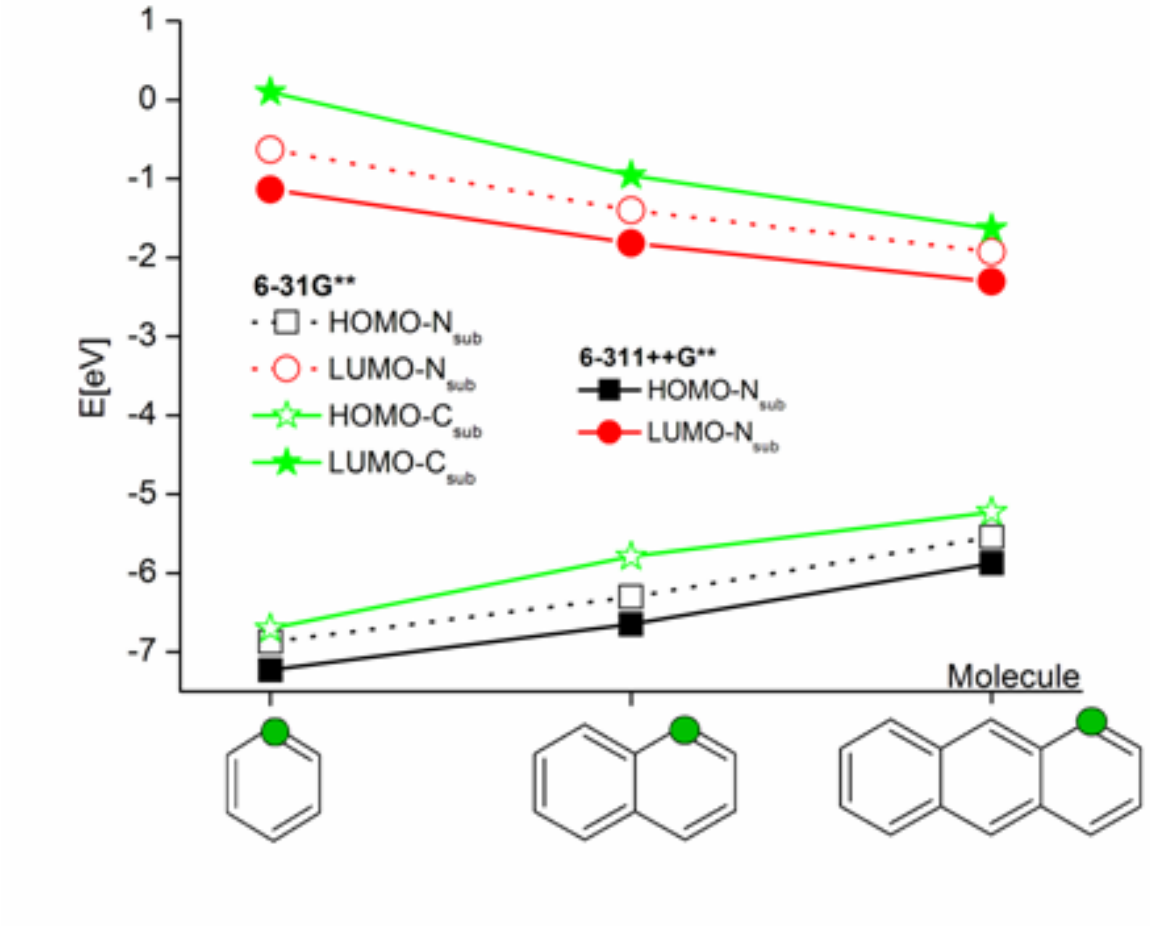


Figure 2. The effect of N/C replacement on HOMO and LUMO energies (in eV) of selected linear polyacenes calculated with B3LYP density functional and two basis sets. For comparison are shown points reported earlier as result of B3LYP/STO-3G$_{mag}$ calculations for traditional acenes. The substitution atom is marked by full circle and individual points were connected for the reader's convenience

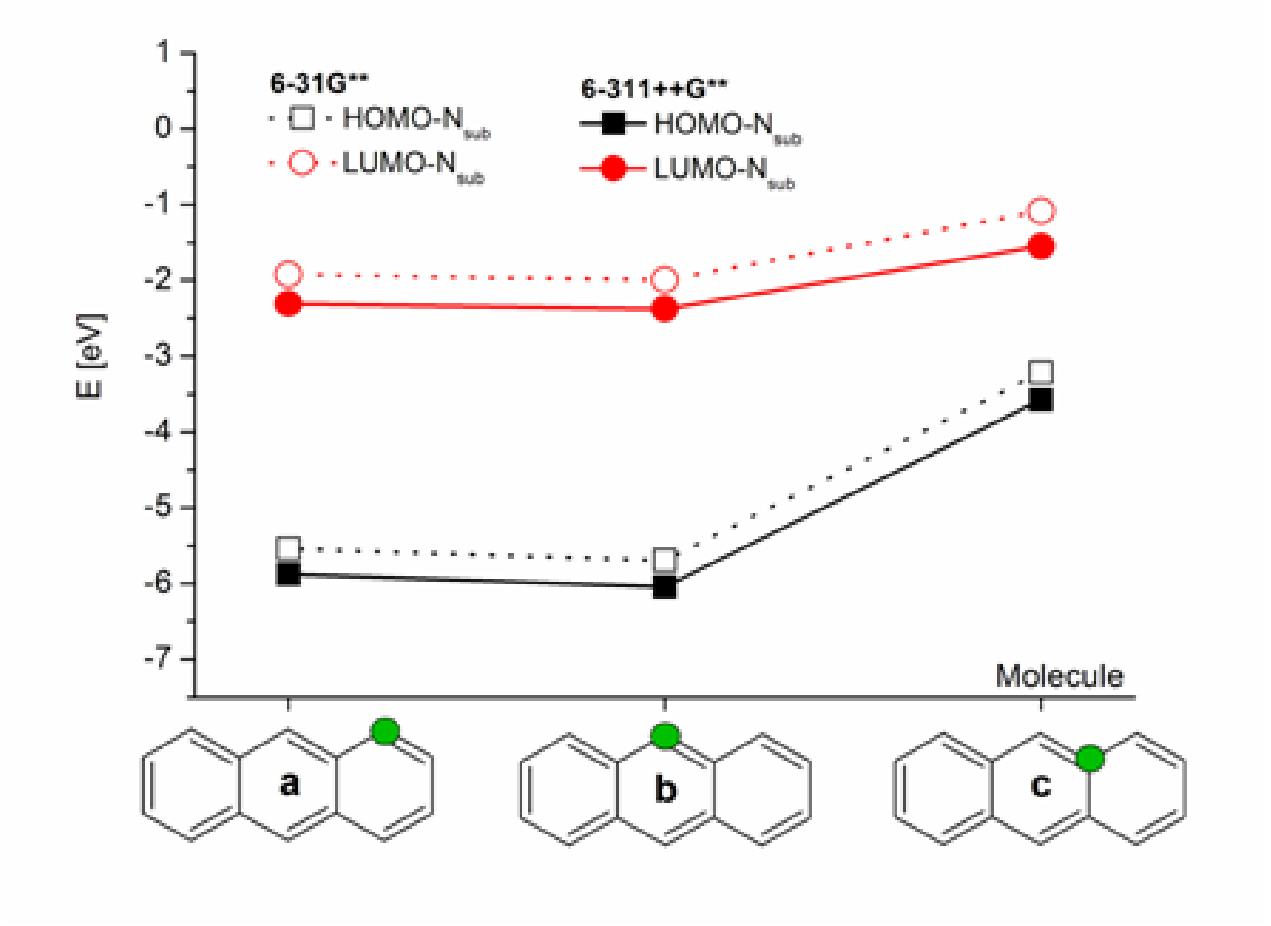


Figure 3. B3LYP calculated HOMO and LUMO energies (E in eV) of selected three membered acene rings as function of N position. Individual points are connected for the reader's convenience

Table 1. B3LYP calculated and experimental HOMO/LUMO gap energies (E_g in eV) for three initial linear acenes (1P, 2P and 3P), their N-substituted analogs and coronene "flake" formed by seven hexagonal rings containing a single nitrogen atom in three different positions (7Pa, 7Pb and 7Pc).

	C – substituted[a]			N-substituted	
Model	6-31G*	STO-3Gel	Exp.	6-31G**	6-311++G**
1P	6.8	6.59	5.96[b]	6.24	6.09
2P	4.83	4.73	4.45[c]	4.90	4.83
3Pa	3.59	3.53	3.45[c]	3.62	3.57
3Pb				3.70	3.67
3Pc				2.13	2.03
7Pa				3.92	3.89
7Pb				1.68	1.68
7Pc				1.68	1.67

a) results from ref. [11]; b) see ref. ; c) see ref. [38]

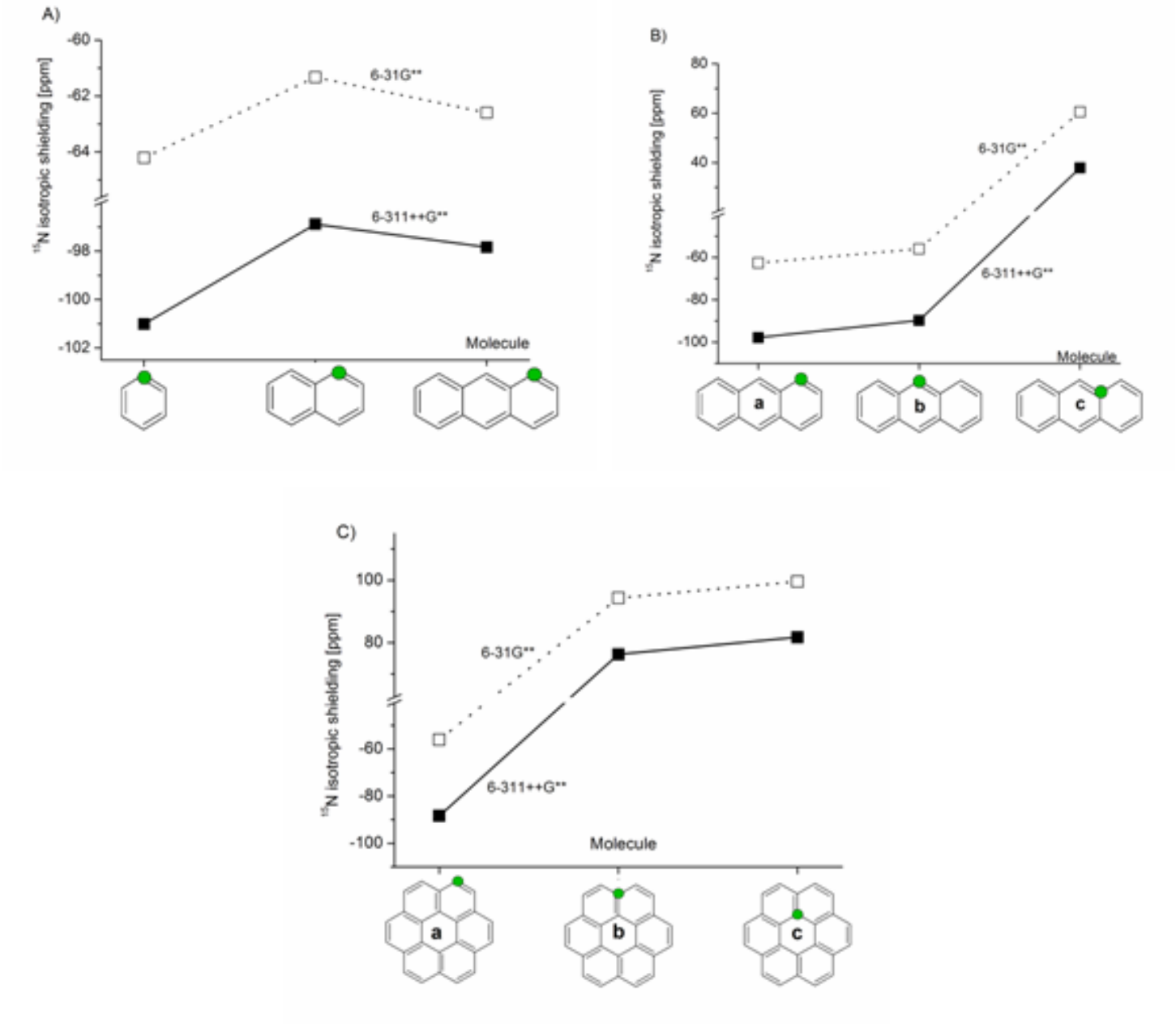


Figure 4. Basis set effect on B3LYP calculated ^{15}N NMR isotropic shieldings in (A) 1P, 2P and 3Pa, (B) 3Pa, 3Pb and 3Pc and (C) coronenes (7Pa, 7Pb and 7Pc)

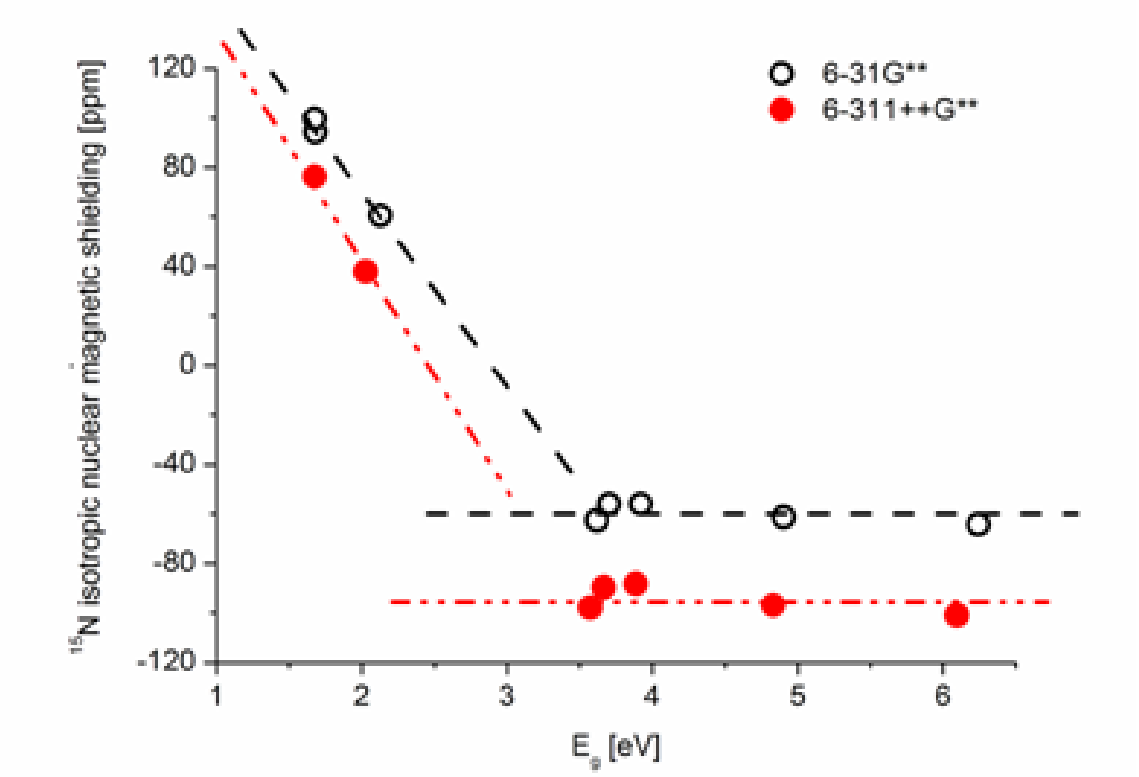


Figure 5. Plot of B3LYP calculated ^{15}N NMR shieldings as function of E_g in the studied systems. Arbitrary trend lines in two ranges of E_g values are shown.

Acknowledgments

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Wnioski:

1. Obliczenia DFT dla modeli N-dopowanych grafenow
2. HOMO/LUMO, NMR
3. Metoda UB3LYP/6-311++G**
4. Przydatne do modelowania wiekszych ukladow

Podziękowania:

1. **ACK Krakow** (oprogramowanie,sprzęt komputerowy i pomoc techniczna).

2. Uniwersytet Opolski, Wydział Chemii

Z Kraju Ryżu, Herbaty i Tajfunów do ... Zakopane'2014

Dziękuję za uwagę