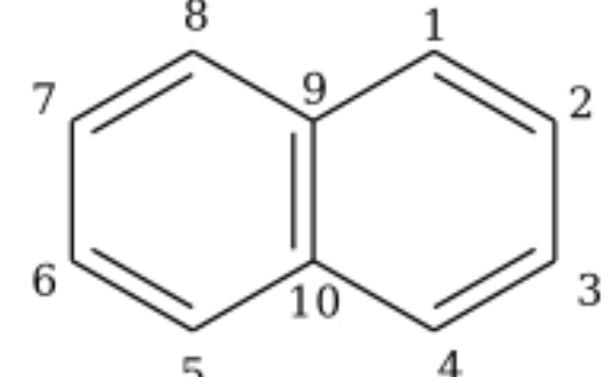


Introduction

Polycyclic aromatic hydrocarbons (PAHs) are some of the most extensively researched compounds for organic photovoltaic (OPV) materials [1]. There has been growing interest in introducing elements such as B, N, Ge, P, O, or S into PAHs, as this innovative strategy is crucial in designing materials with tailored properties. Doping is a versatile strategy for enhancing the properties of organic compounds, making it attractive for the customization of organic electronics. Incorporating boron and nitrogen atoms into a molecule allows for adjustable bandgap tuning, either increasing or decreasing. This tunability is crucial for designing materials with desired optical and electronic properties [2]. The boron and nitrogen atoms, forming an isoelectronic pair resembling two carbon atoms, have been utilized to replace carbon-carbon units with boron-nitrogen units in naphthalene [3], yielding all 23 possible BN-doped isomers. The electronic structure of a few isomers has been studied so far, but there remains a significant gap in developing a comprehensive understanding of the impact of BN/CC exchange on the electronic structure, as outlined in this poster. In addition, current research highlights that studies on the OPV applications of BN-doped systems are largely unexplored.



The specific sites of each carbon in the naphthalene ring system.

Methodology

The methods incorporated in these calculations were:

- CCSD
- CCSD(T)
- EOM-pCCD-LCCD
- EOM-pCCD-LCCSD
- IP-EOM-fpCCD
- IP-EOM-fpCCSD
- IP-EOM-pCCD
- DIP-EOM-pCCD

Software:

- All the molecular electronic structure calculations with pCCD were conducted using the developer version of the PyBEST v2.0.0-dev0 software [4].
- MOLPRO package [5] was used for canonical coupled-cluster calculations.
- The optimization of molecular structures was performed using the TURBOMOLE software package, and molecular structures were optimized with the BP86 functional and def2-TZVP basis sets. After optimization, vibrational frequency calculations were conducted, confirming that all the structures were energy minima with no imaginary frequencies.

Considered geometries:

- Frozen: Swap atoms from naphthalene;
- Optimized: Optimization for each BN position.

Other parameters:

- Basis set: cc-pVDZ and cc-pVTZ basis sets designed by Dunning [6];
- 1s orbitals for C, N, and B are frozen during pCCD orbital optimization.

The pCCD ansatz:

- is size-extensive by construction,
- includes strong correlation,
- is improved by a simultaneous orbital optimization.

The pCCD wave function is

$$|\Psi_{\text{el}}^{\text{pCCD}}\rangle = e^{\hat{T}_p} |\Phi_0\rangle, \quad (1)$$

where $|\Phi_0\rangle$ is some reference determinant and \hat{T}_p is a cluster operator that excites electron pairs,

$$\hat{T}_p = \sum_i^{\text{occ. virt.}} \sum_a c_i^a a_a^\dagger a_i^\dagger a_i a_i, \quad (2)$$

where index a and i refer to virtual and occupied spin orbitals, respectively.

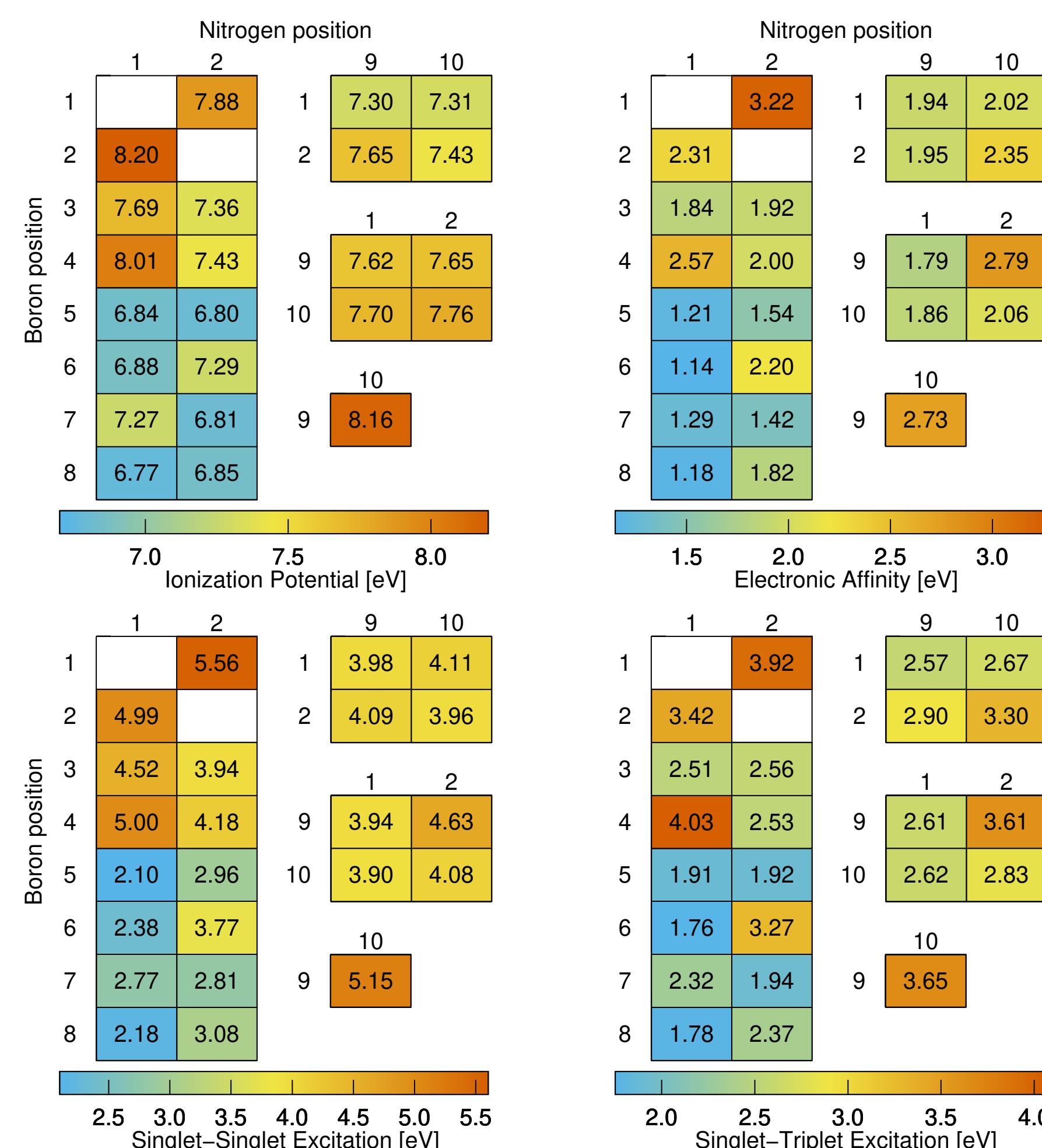
CC-based method accuracy

Table 1 Ionization potentials (in eV) obtained from several computational approaches and experimental values [7]. Mean unsigned error (MUE) and root mean square error (RMSE) using experimental values as reference.

System	IP-EOM-fpCCD	IP-EOM-fpCCSD	CCSD	CCSD(T)	Exp.
Benzene	9.175	9.137	9.281	9.354	9.243
Borazine	9.885	9.917	9.947	9.953	9.880
Naphthalene	8.178	8.068	7.972	7.942	8.144
BN-1,2-Naphthalene	8.212	8.197	8.188	8.266	8.450
BN-1,9-Naphthalene	7.699	7.764	7.486	7.550	7.780
BN-9,1-Naphthalene	7.358	7.312	7.184	7.252	7.440
BN-9,10-Naphthalene	8.258	8.158	8.020	7.969	8.240
MUE	0.075	0.100	0.187	0.180	—
RMSE	0.104	0.123	0.209	0.190	—

Considering all 23 isomers an excellent agreement is observed, with the MUE and RMSE between CCSD(T) and IP-EOM-fpCCSD are 0.094 and 0.101 eV, respectively.

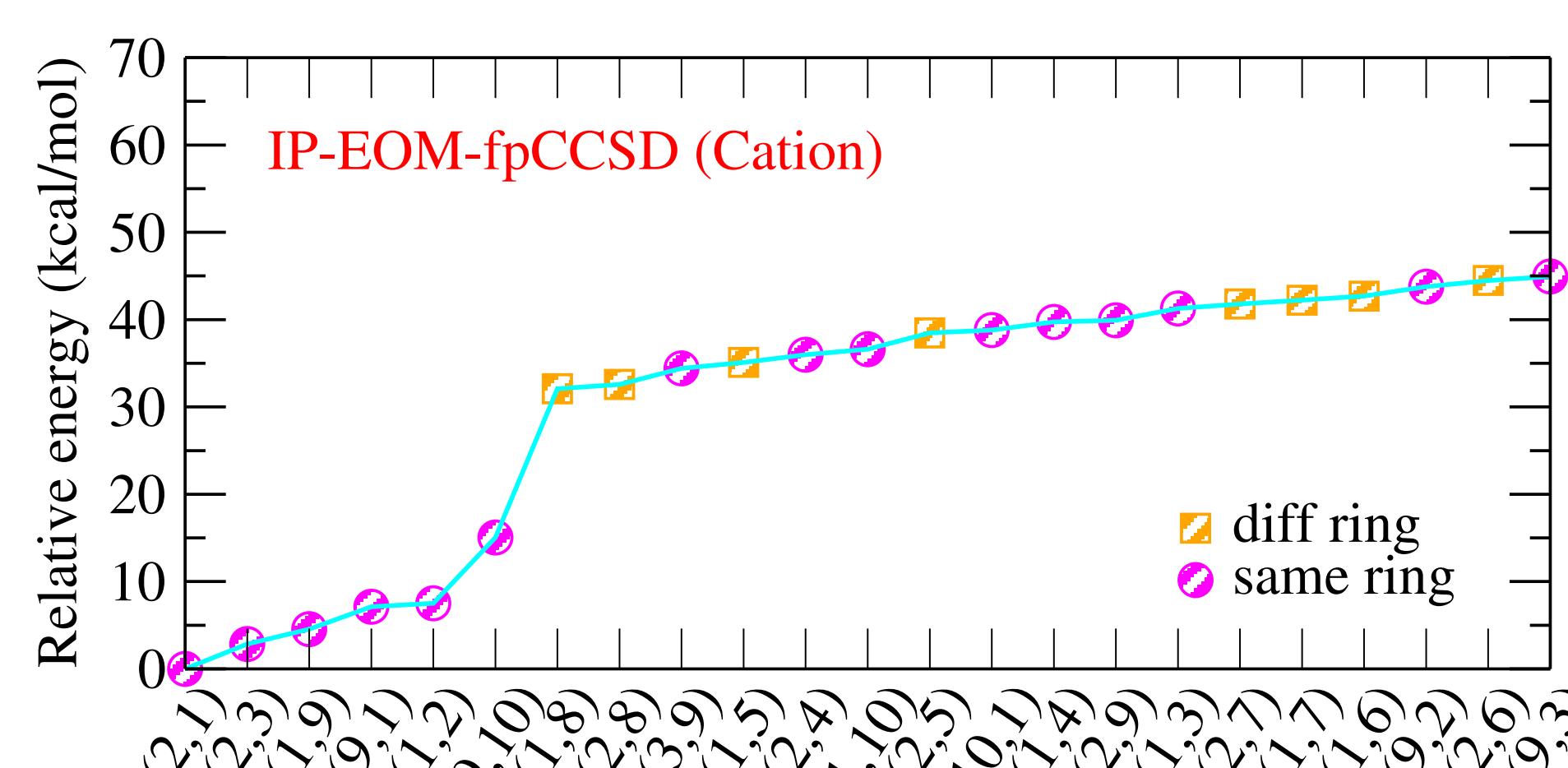
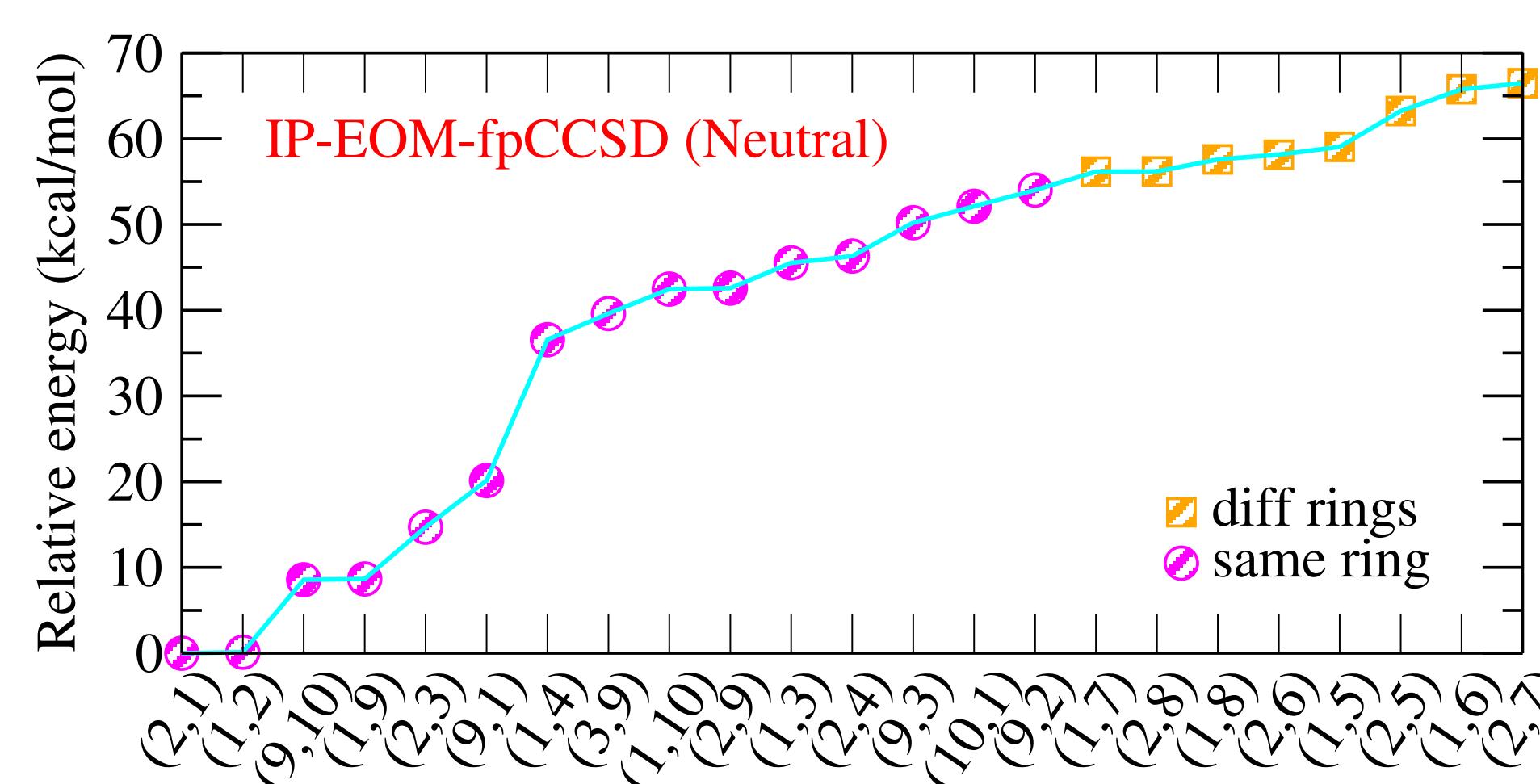
Data interpretation



All properties explored follow a similar pattern, the system where the heteroatoms share the same ring has a higher value.

Graphical analysis

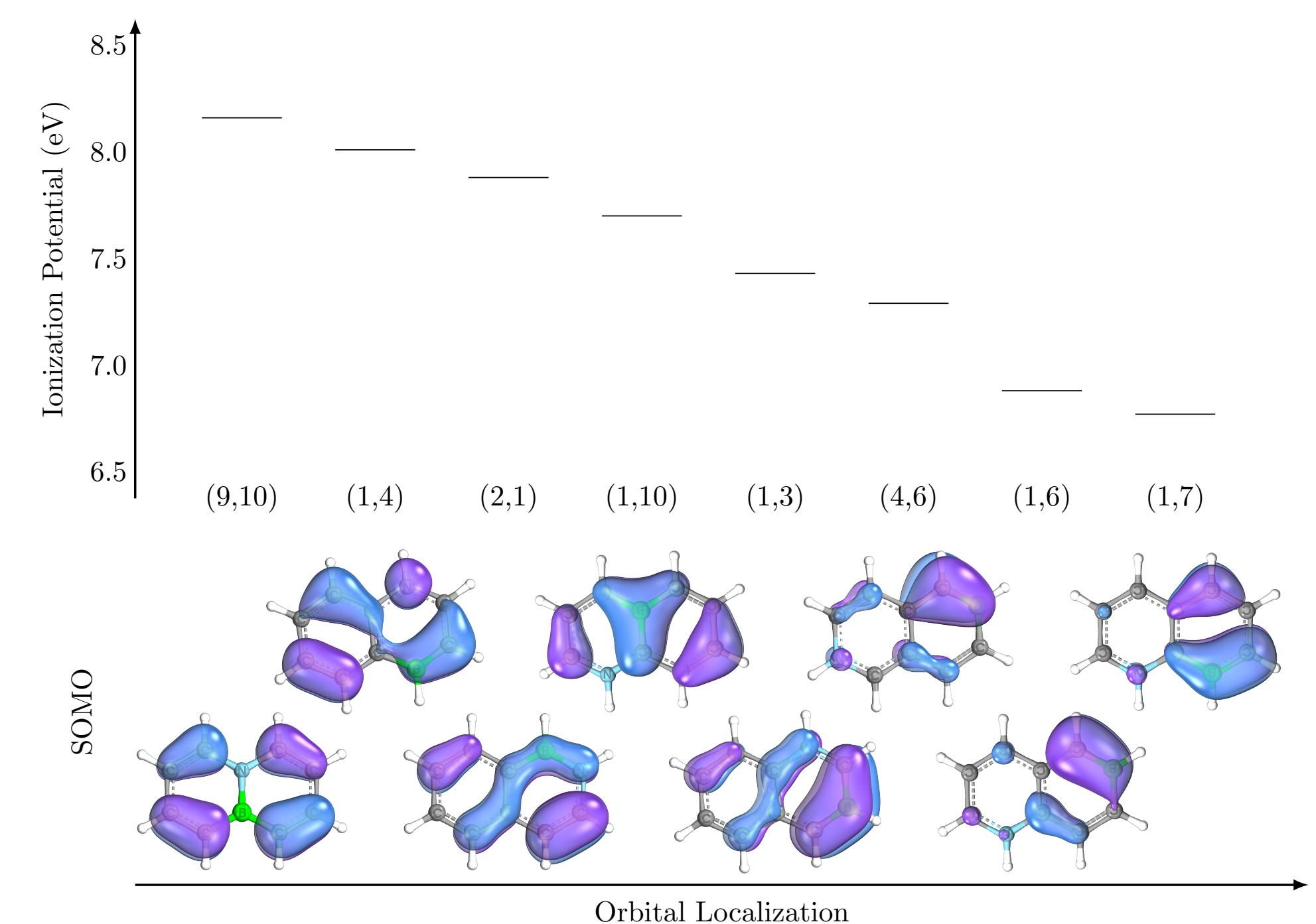
Fig.1 Relative energies of the BN-doped naphthalene system, with the neutral state shown at the top and the cationic state at the bottom.



The separation of energy among isomers is significantly greater in the neutral state compared to the cationic state.

SOMO localization in the cation

Fig.2 Ionization potential of the BN-doped naphthalene and below their respective single-occupied molecular-orbital (SOMO).



The IP decreases with the localization of the SOMO. Isomers with higher IP, such as (9,10), have SOMO resembling pure Naphthalene, while those with lower IP, like (1,7), are closer to the neutral boron-doped Naphthalene SOMO.

Conclusions

- (1) Our results demonstrate good agreement among the fpCCD, fpCCSD, and CCSD(T) methods, which closely align with experimental values.
 - (2) The calculation results show higher ionization potential, singlet-singlet, and singlet-triplet values for systems where both heteroatoms in the same ring compared to those in different rings.
 - (3) Analysis of molecular orbitals shows that, with B and N atoms confined in the same ring, the SOMO usually exhibits a delocalized character. In contrast, when they occupy distinct rings, the SOMO is mainly localized in the ring that contains the B atom.
 - (4) The results of this work show that some fundamental properties of the smallest member of PAHs, naphthalene, can be tuned by varying the position of the BN unit within the molecule.
- We hope that the established relationships will guide experimental chemists to synthesize and precisely customize organic photovoltaic (OPV) materials with optimal and tailored properties.

Acknowledgement

The authors acknowledge financial support from the Center of Excellence, Poland. A.L. acknowledges financial support from Academia Scientiarum Thoruniensis(AST).



The PyBEST code is available on Zenodo at <https://zenodo.org/records/10069179> and on PyPI at <https://pypi.org/project/pybest/>

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