Aromaticity, HOMO-LUMO Energy Gaps and Triplet State Energies of Boron-Nitrogen Doped Coronene

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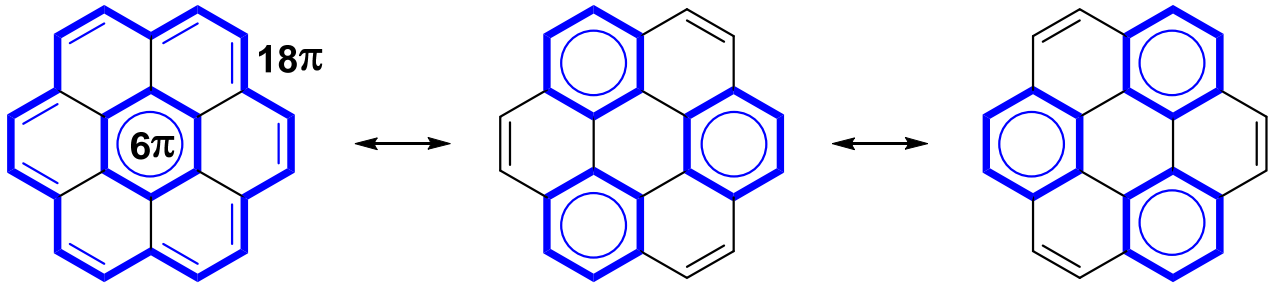
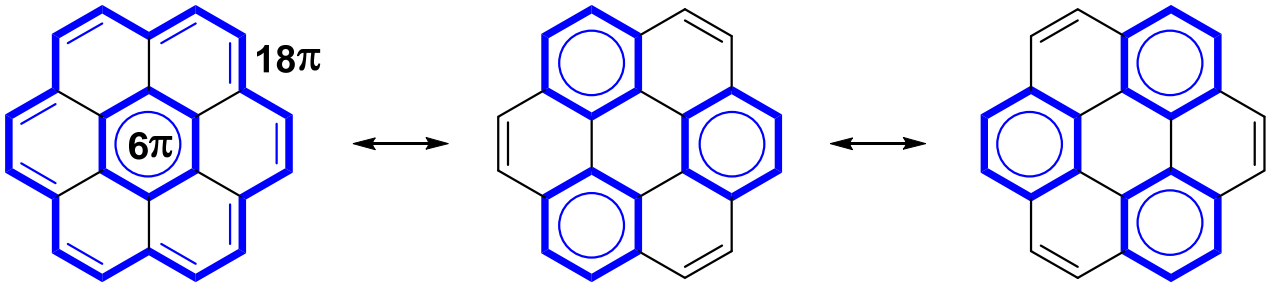
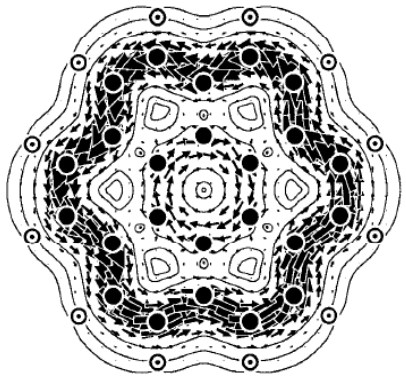
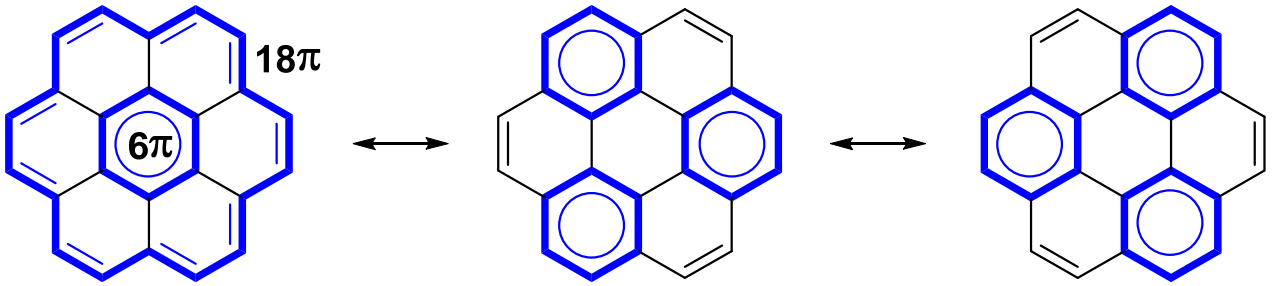
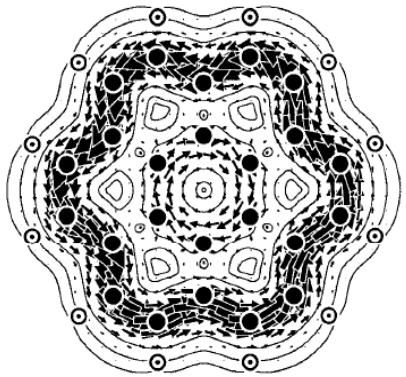

18π
6π

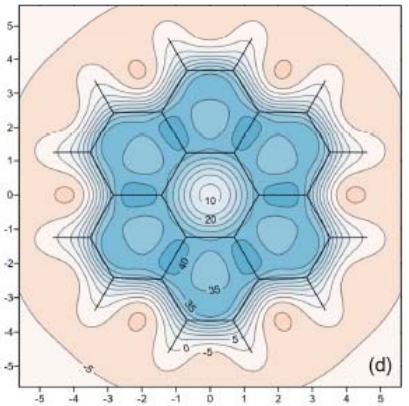




E. Steiner, P. W. Fowler, L. W. Janneskens, ACIE 2001, 40, 362.
E. Steiner, P. W. Fowler, JPCA 2001, 105, 9553.







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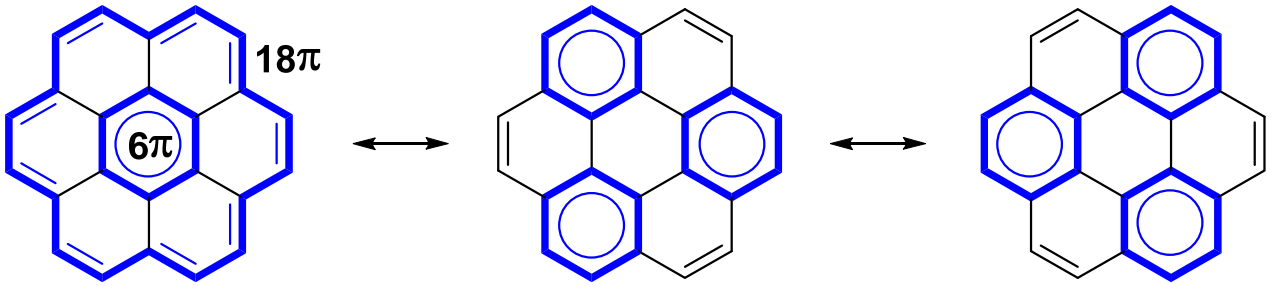
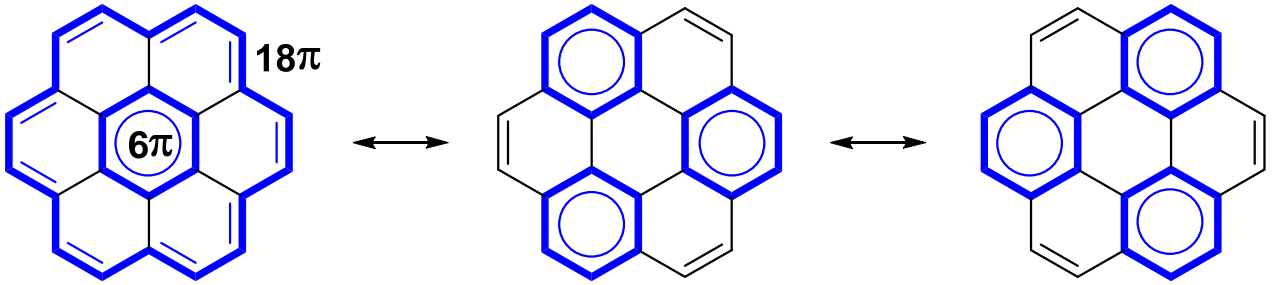
E. Steiner, P. W. Fowler, L. W. Janneskens, ACIE 2001, 40, 362.
E. Steiner, P. W. Fowler, JPCA 2001, 105, 9553.

P. Karadakov, Chemistry 2021, 3, 861.



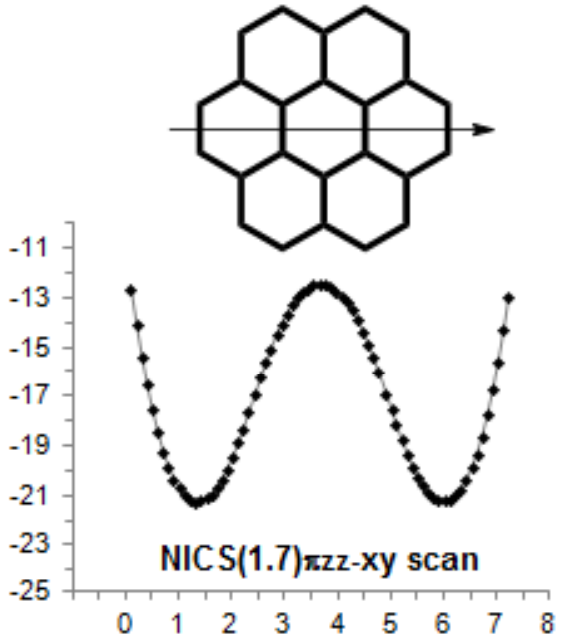
A. Kumar, M. Duran, M. Solà, JCC 2017, 38, 1606.



A. Kumar, M. Duran, M. Solà, JCC 2017, 38, 1606.

ωB97XD/6-311+G(d,p)	inner	outer	perimeter
HOMA	0.657	0.782	0.746
FLU	0.0295	0.0183	0.0163
PDI	0.0294	0.0570	/
$EDDB_P$	2.3764 (40%)	2.4948 (42%)	7.3593 (41%)
$NICS(1.7)_{\pi zz}$	-12.5	-21.2	/

M. Baranac-Stojanović, M. Stojanović, J. Aleksić, NJC 2024, 48, 14277.

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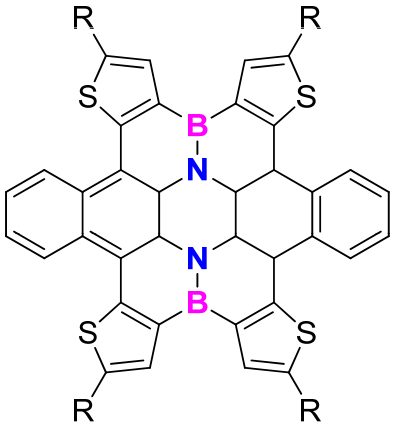
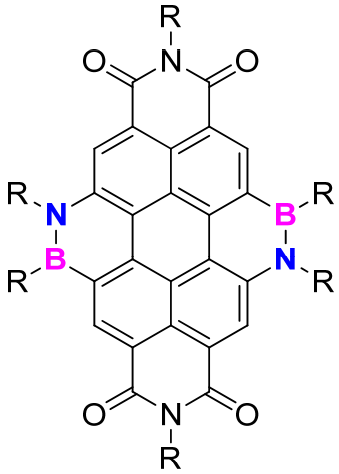
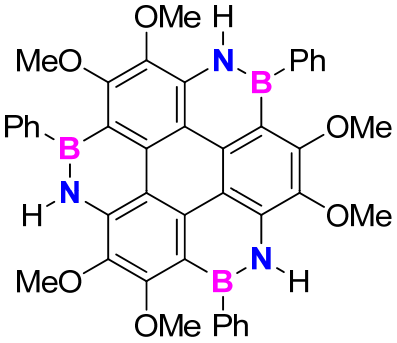


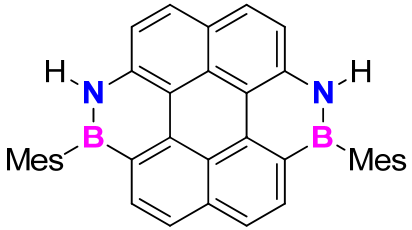
X. Y. Wang et al.,
JACS 2014, 136, 3764.



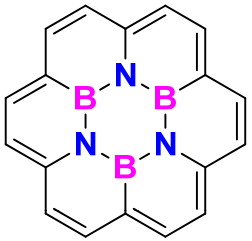
J. Hoffmann et al.
JMCC 2021, 9, 13926.



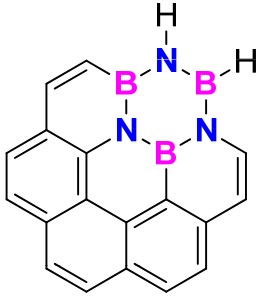
G. Li et al.
OL 2015, 17, 560.



Z. Jiang et al.
OL 2022, 24, 1017.



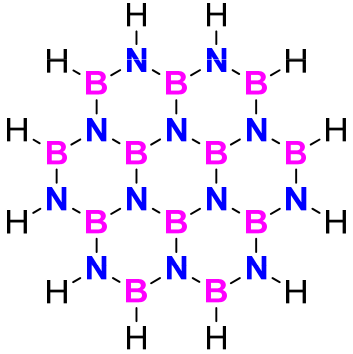
1



2

L. Türker, PAC 2012, 32, 61.

HOMO-LUMO gap: **2** > **1**

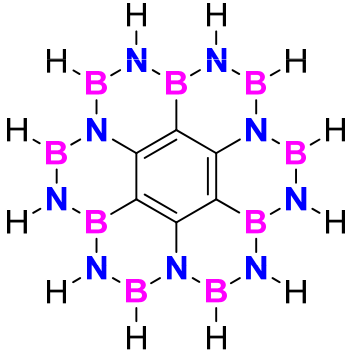


3

A. L. Sobolewski, W. Domcke,

PCCP 2023, 25, 21875.

3: Inverted S_1-T_1 energy gap.



4

S. Sanyal, A. K. Manna, S. K. Pati,

JMCC 2014, 2, 2918.

NICS(0), NICS(1), NICS(1)$_{zz}$

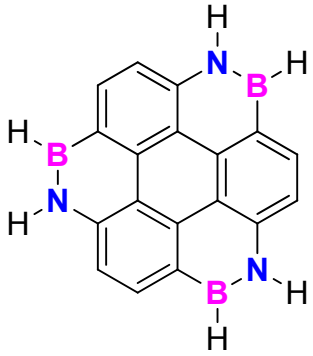
4: Central ring more aromatic than in coronene. BN rings less aromatic or antiaromatic.

E. Steiner, P. W. Fowler, R. G. Viglione, R. Zanasi, CPL 2002, 355, 471.

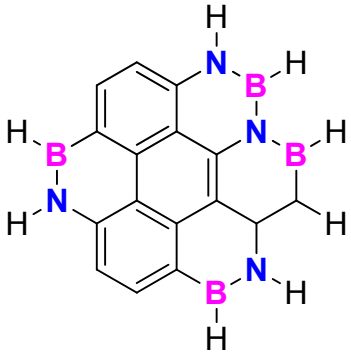
1: 18 π-electron diatropic circulation.

2: Phenanthrene-like current in the carbon-only region.

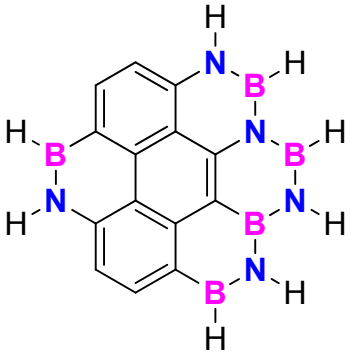
1-3: Localized currents on the nitrogen atoms.



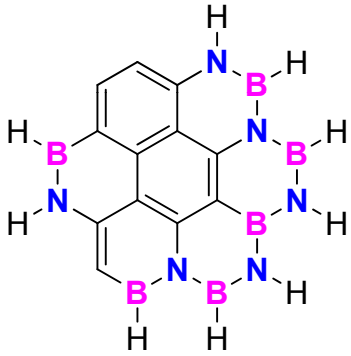
Cor-3BN



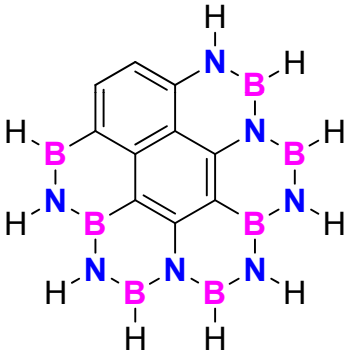
Cor-4BN



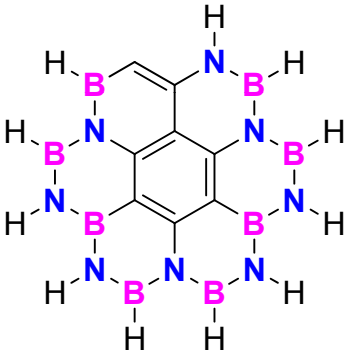
Cor-5BN



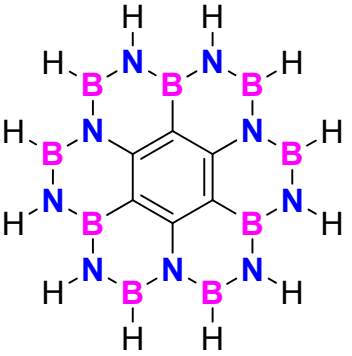
Cor-6BN



Cor-7BN



Cor-8BN



Cor-9BN

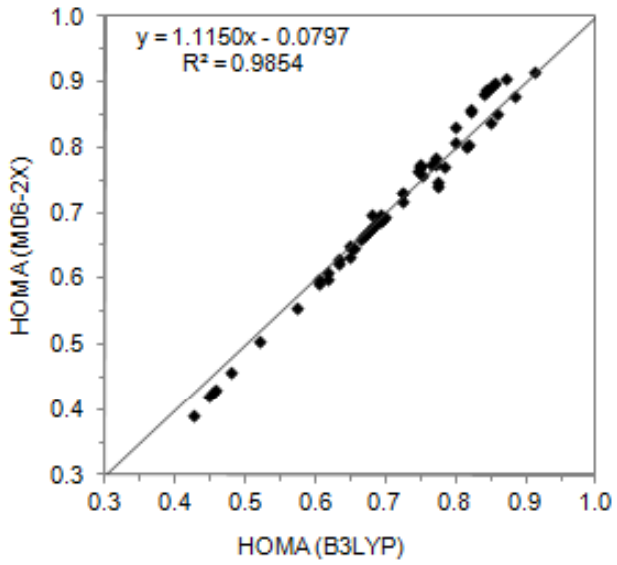
HOMA, FLU, PDI, $EDDB_P$, $NICS(1.7)_{\pi zz}$-xy scan

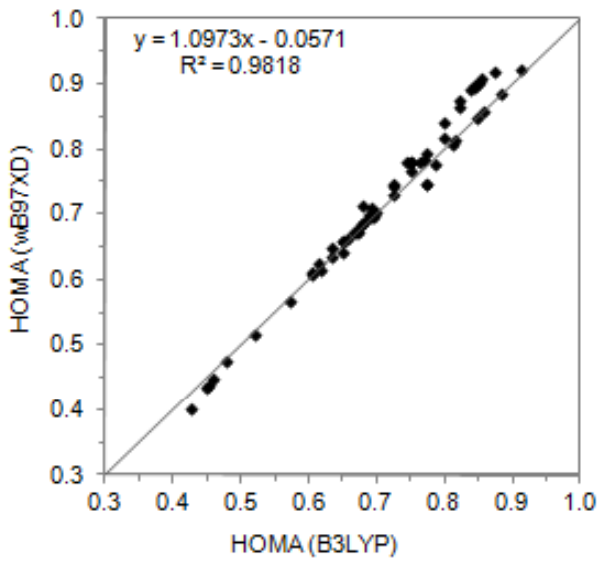
B3LYP-D3(BJ), M06-2X, ωB97XD

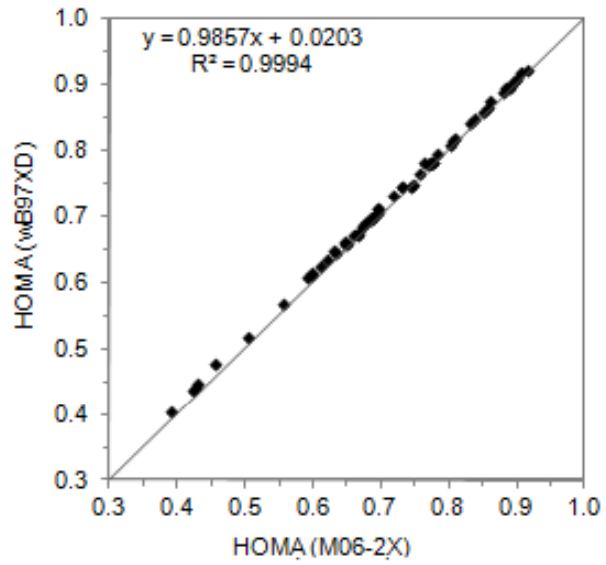
6-311+G(d,p)

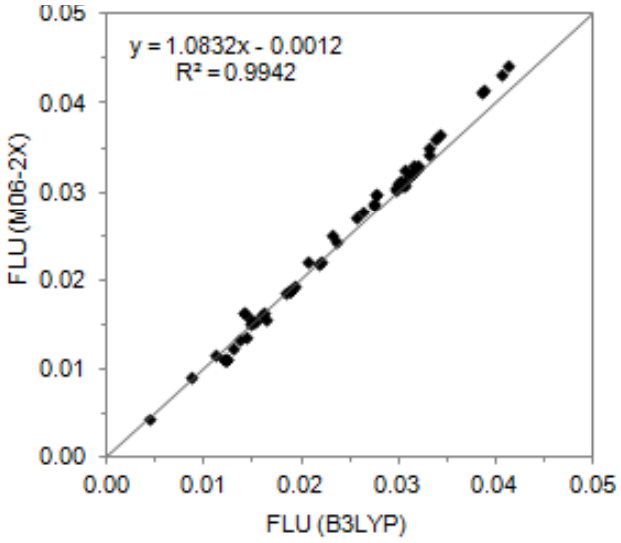
M. Baranac-Stojanović, M. Stojanović, J. Aleksić, NJC 2024, 48, 14277.

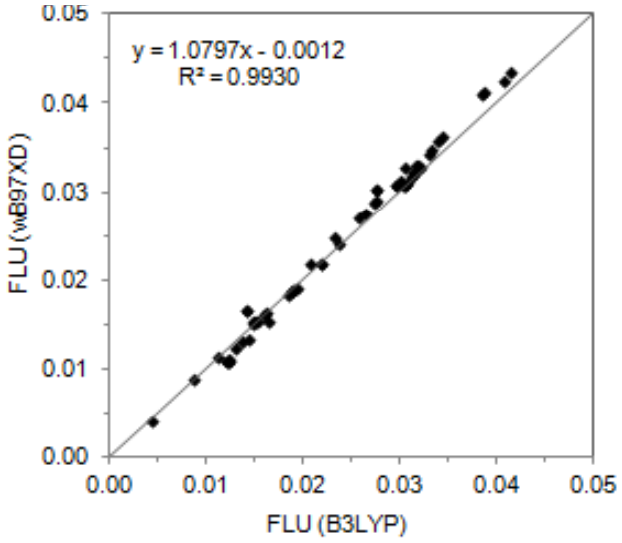
Correlations between different functionals

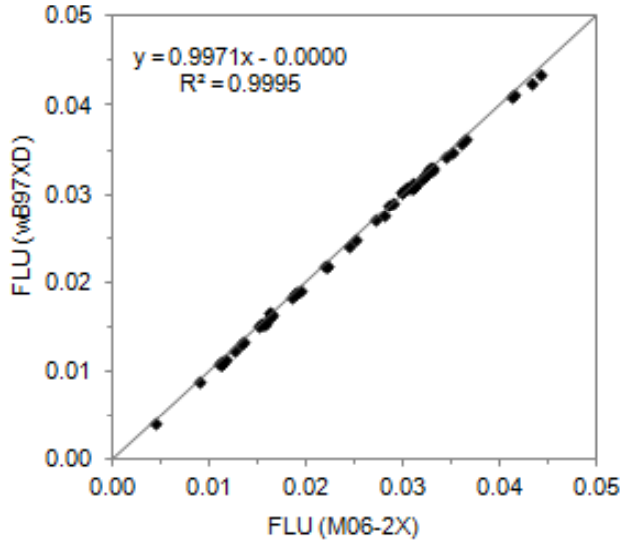




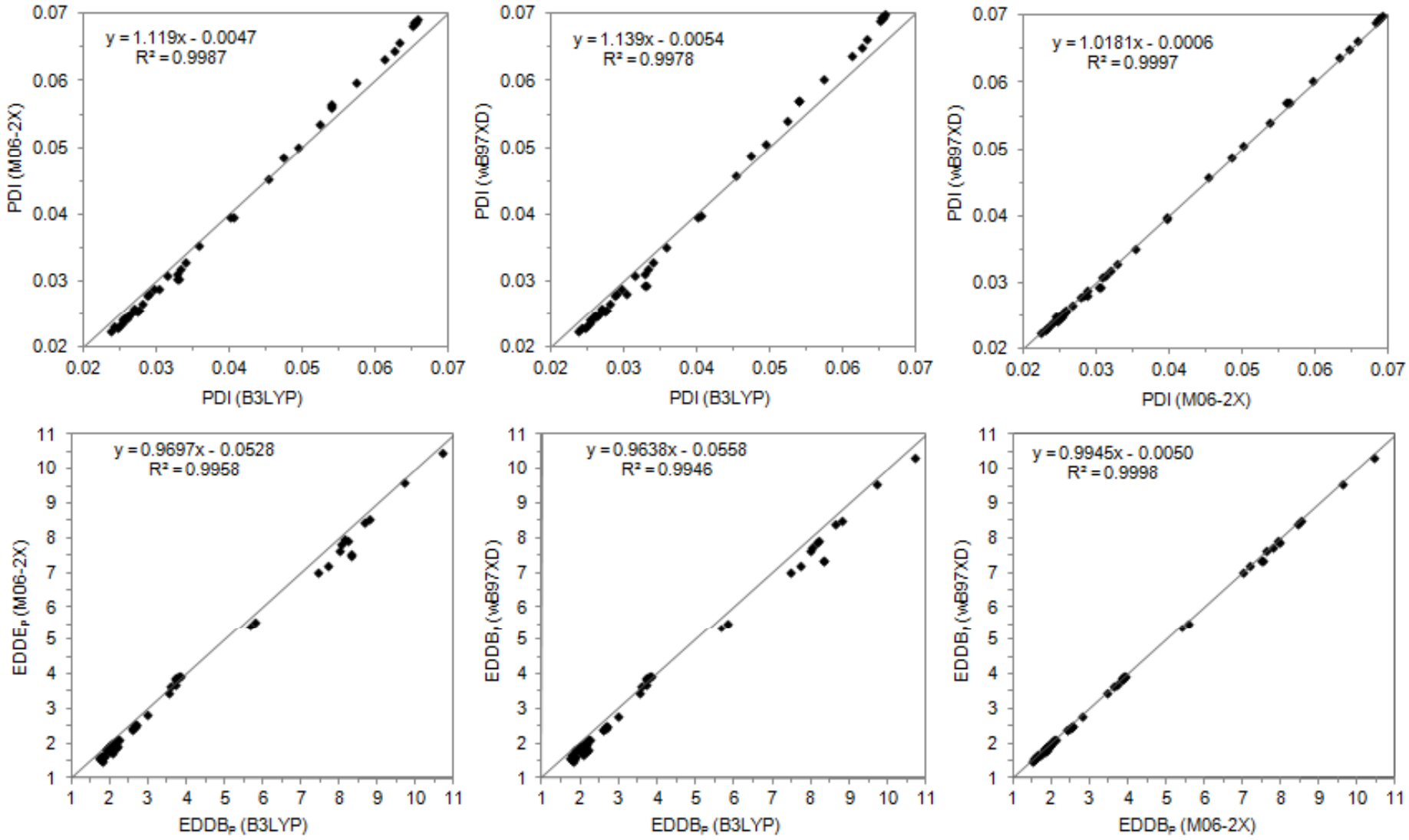




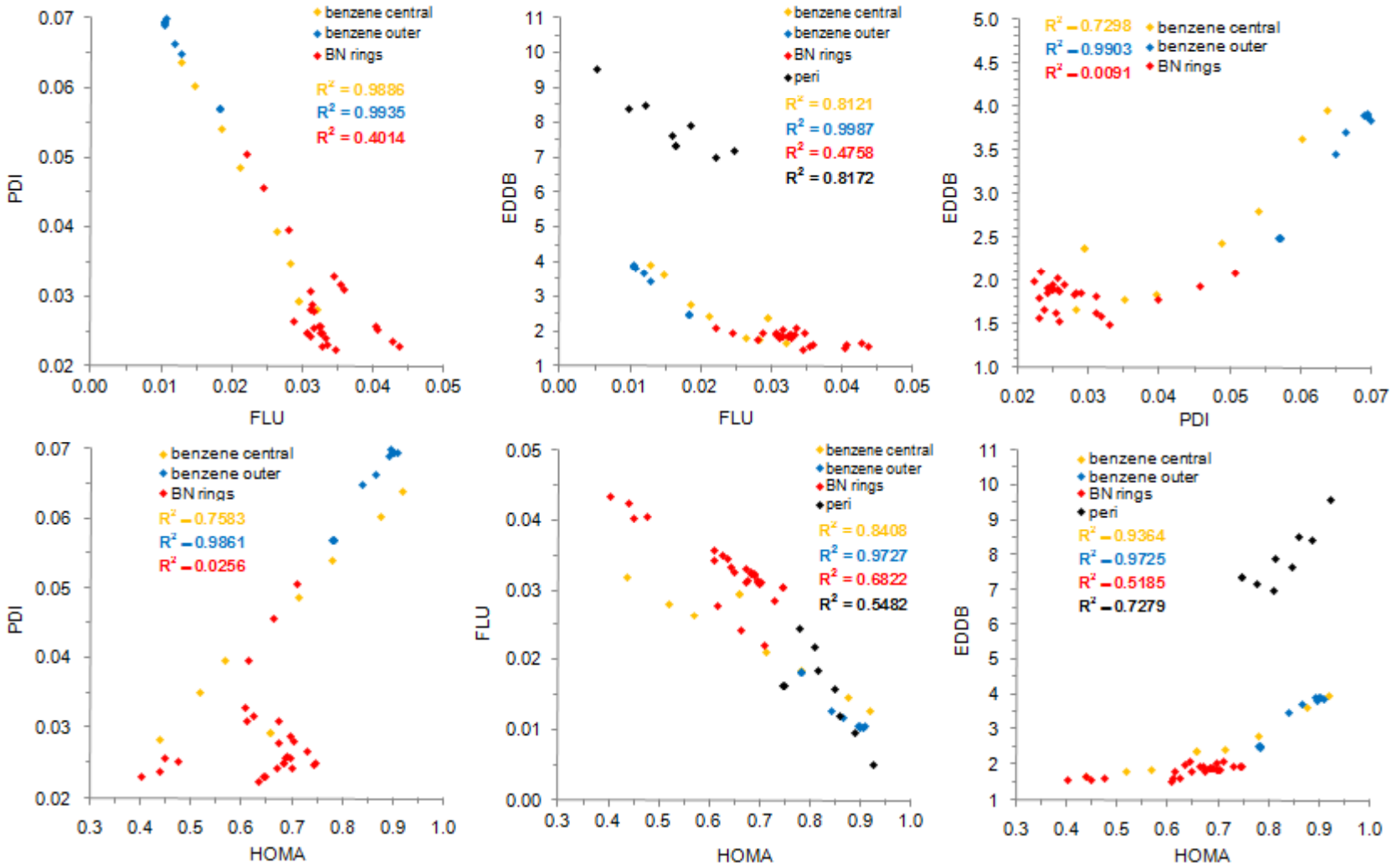




Correlations between different functionals

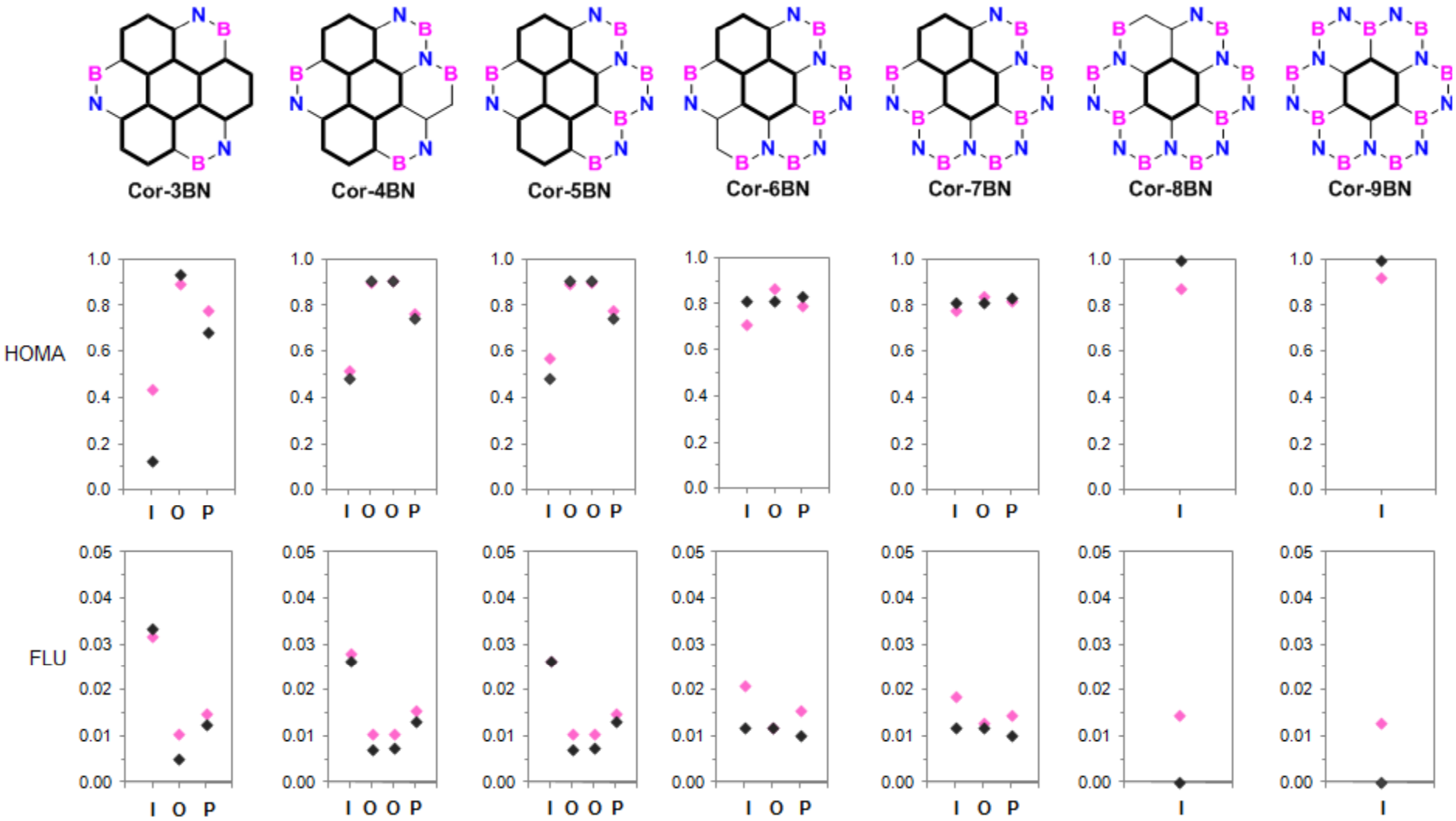


Correlations between different aromaticity indices (ωB97XD/6-311+G(d,p))



	PDI/FLU	EDDB/FLU	EDDB/PDI	PDI/HOMA	FLU/HOMA	EDDB/HOMA
Outer benzene	0.9935	0.9987	0.9903	0.9861	0.9727	0.9725
Central ring, with Cor	0.9886	0.8121	0.7298	0.7583	0.8408	0.9364
Central ring, without Cor	0.9989	0.9364	0.9230	0.9981	0.9991	0.9367
BN rings	0.4014	0.4758	0.0091	0.0256	0.6822	0.5185
Molecular perimeter	/	0.8172	/	/	0.5482	0.7279

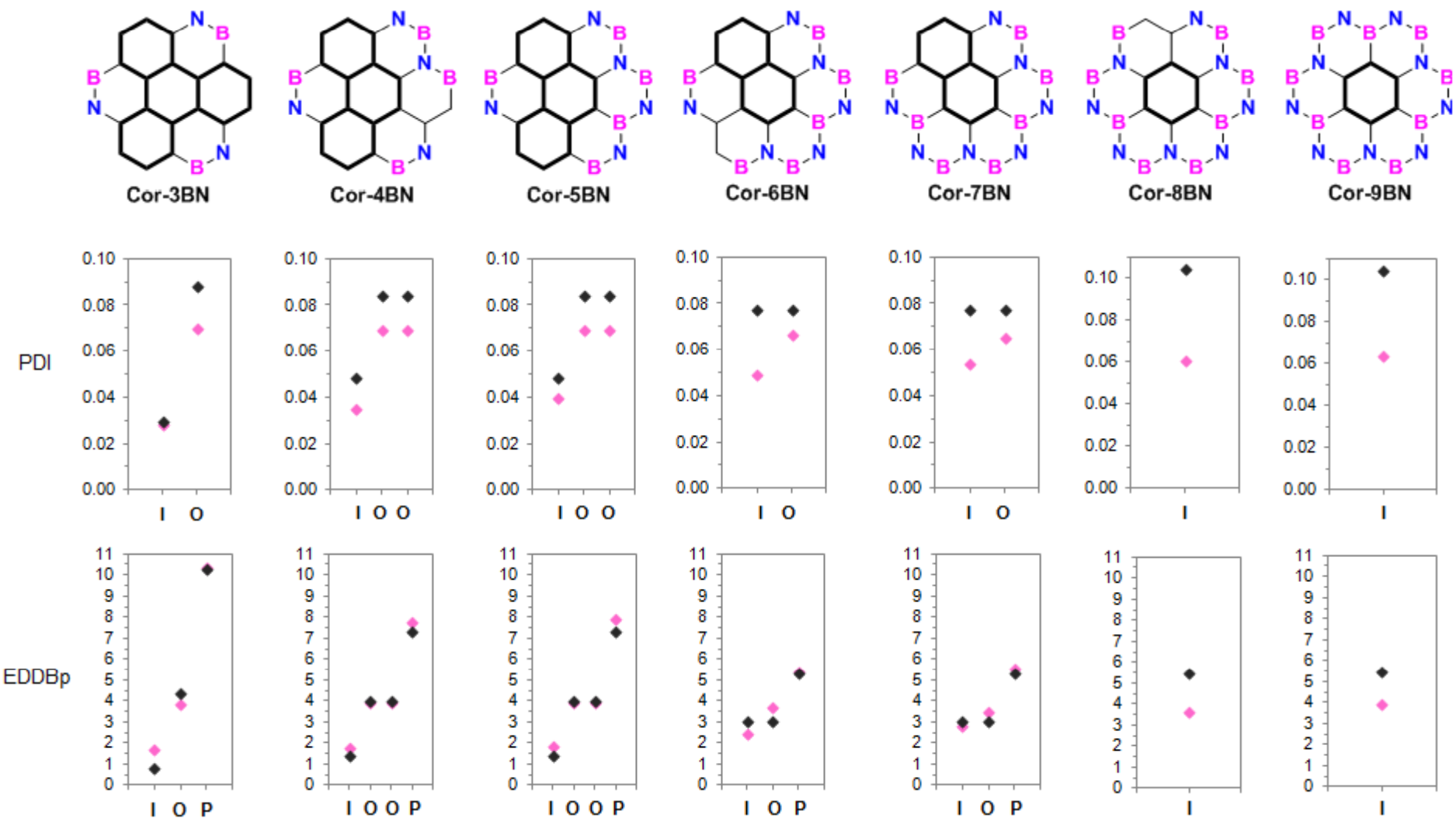
Can BN substitution isolate carbocyclic subunits?



Black dots: Isolated carbocycles, triphenylene, phenanthrene, naphthalene and benzene.

Pink dots: Carbocyclic subunits in BN-coronenes.

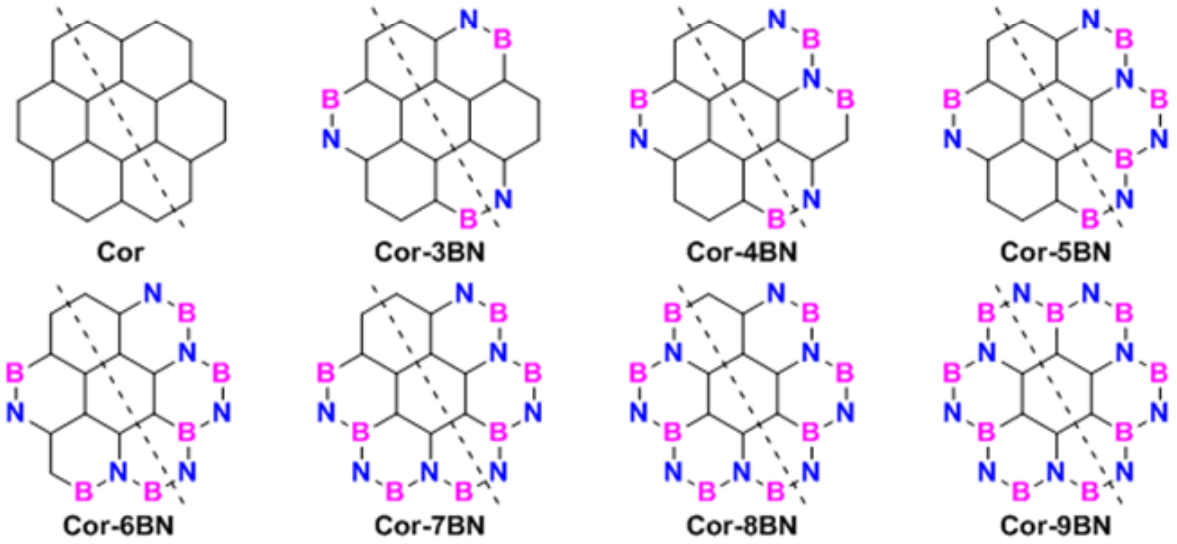
Can BN substitution isolate carbocyclic subunits?

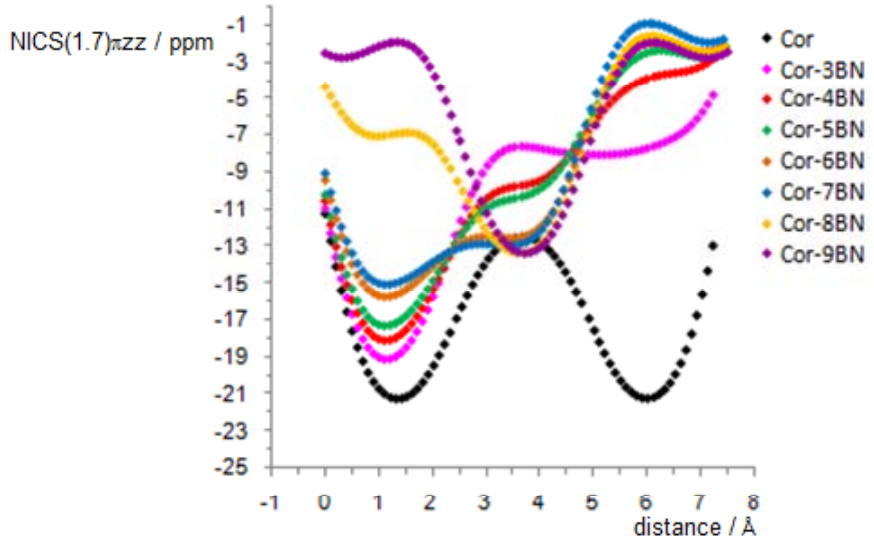


Black dots: Isolated carbocycles, triphenylene, phenanthrene, naphthalene and benzene.

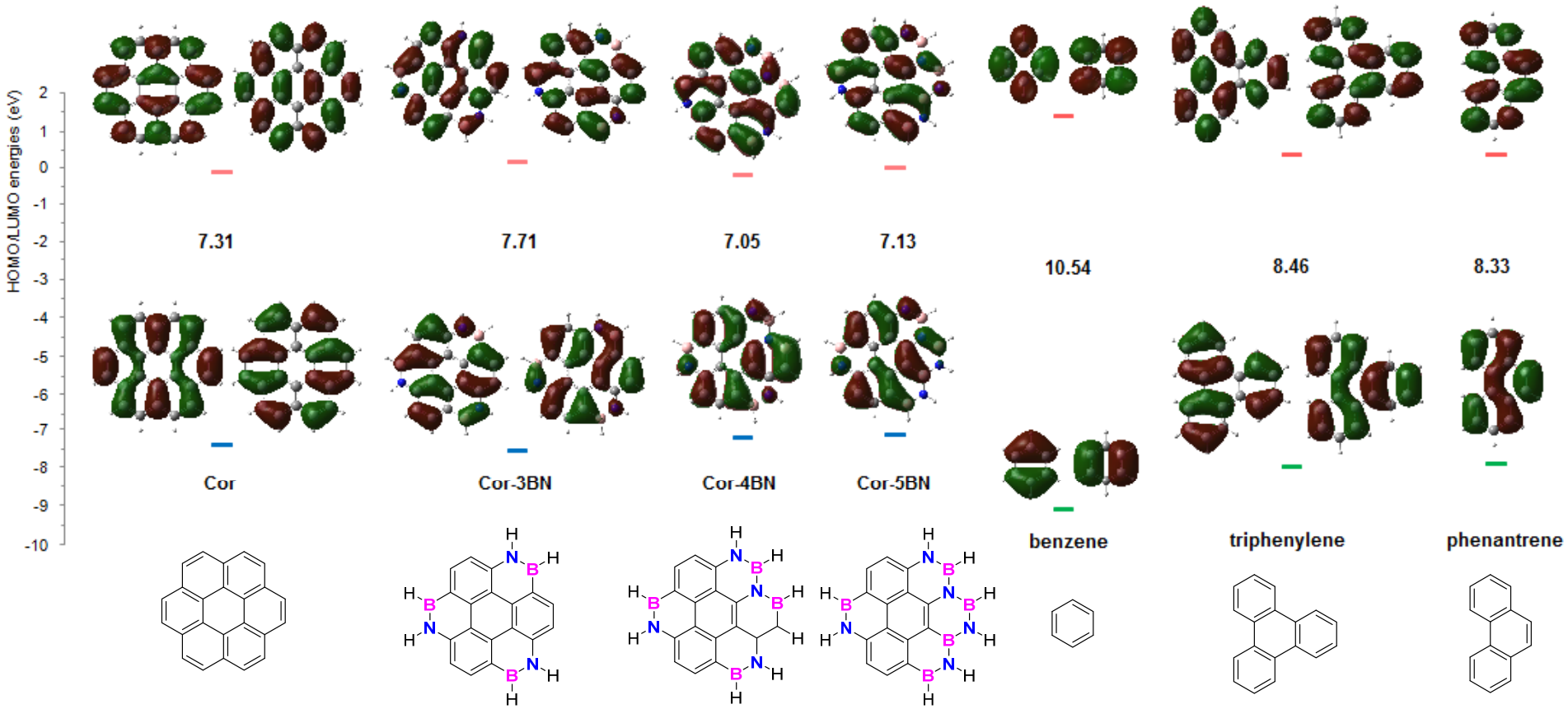
Pink dots: Carbocyclic subunits in BN-coronenes.

What do they affect?

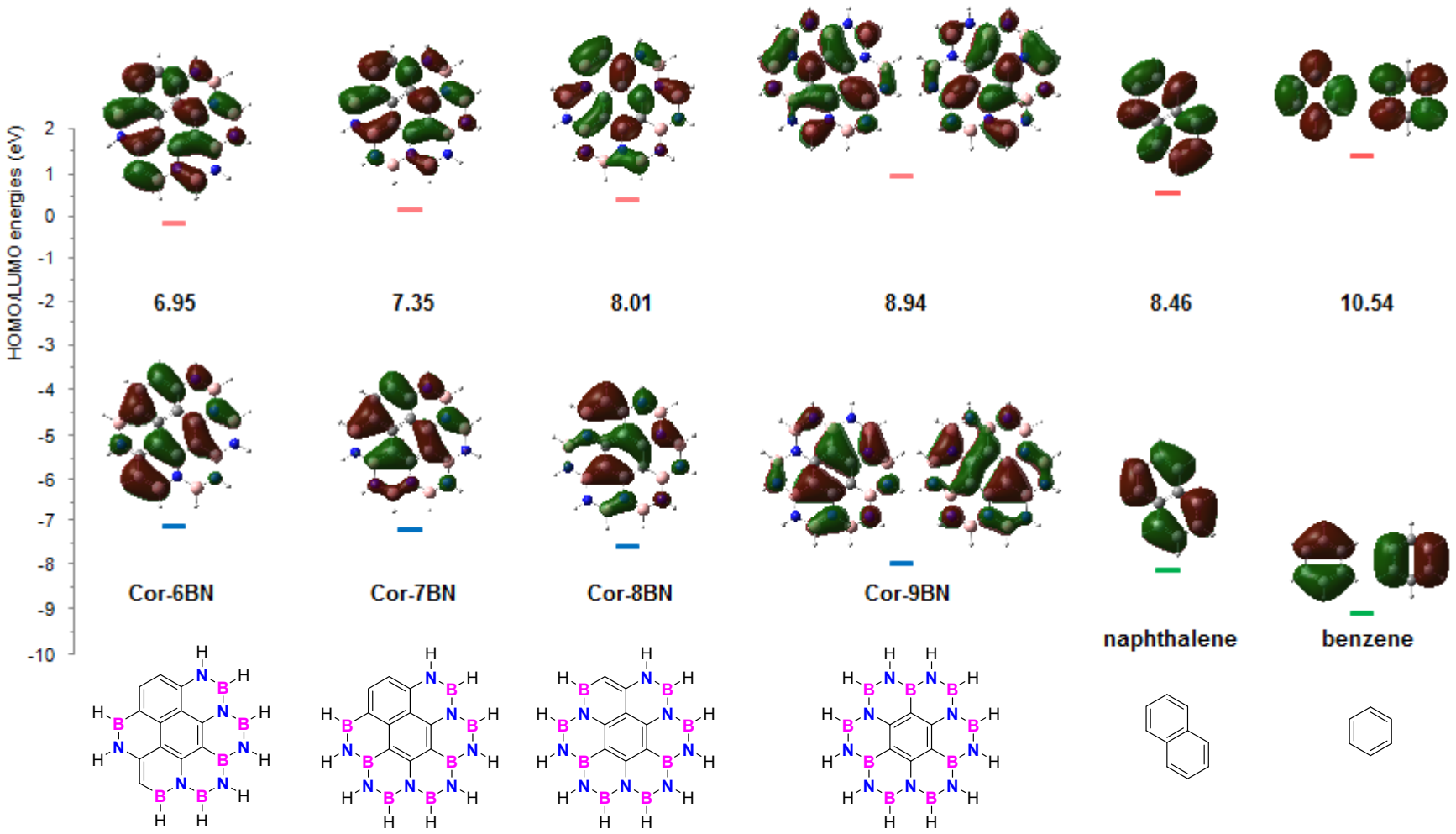




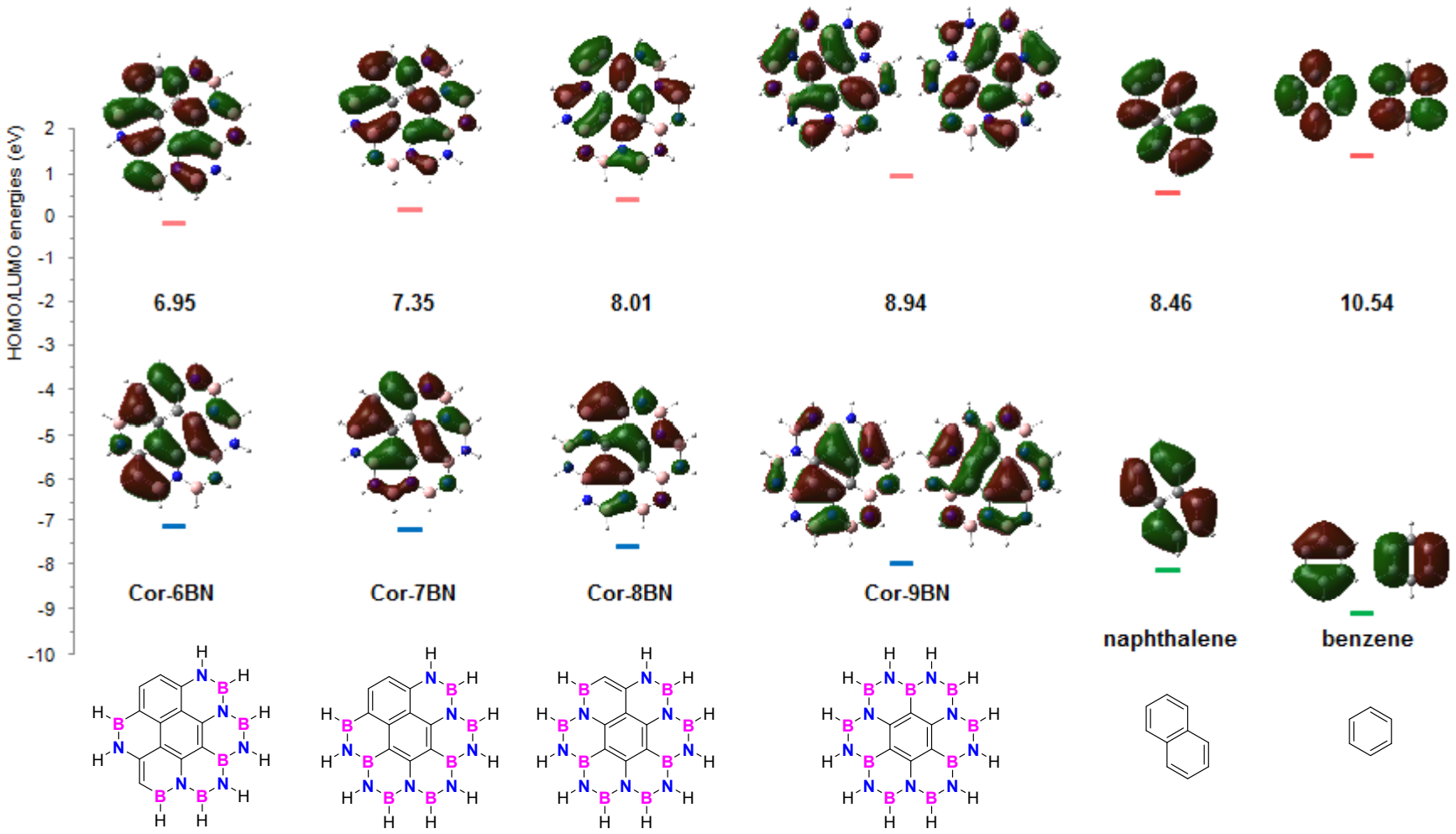
What do they affect?



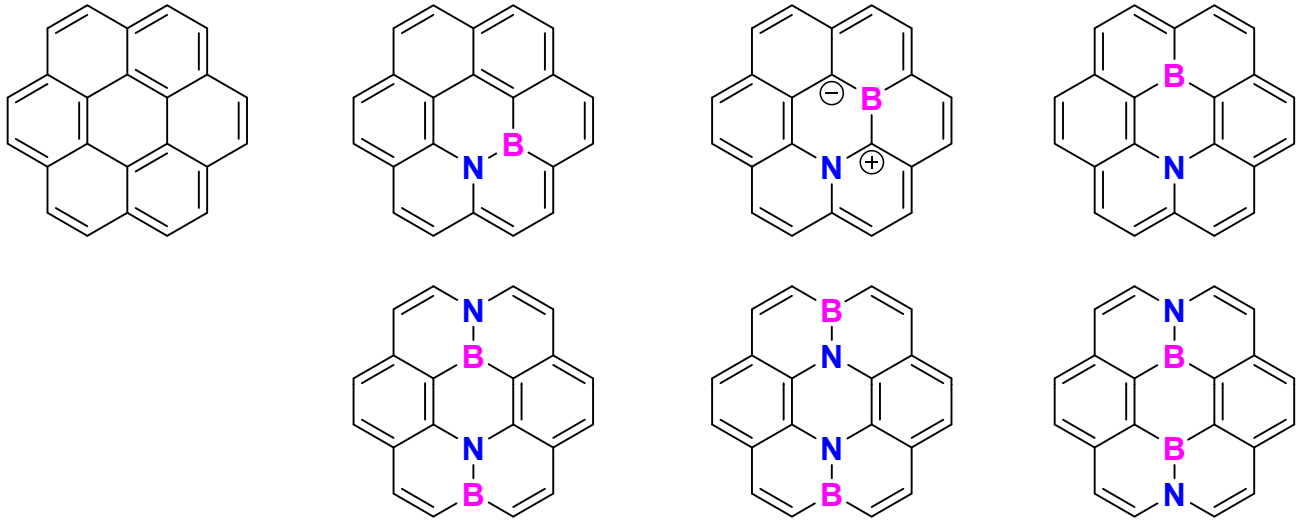
What do they affect?



What do they affect?



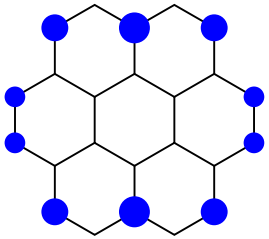
	Cor	Cor-3BN	Cor-4BN	Cor-5BN	Cor-6BN	Cor-7BN	Cor-8BN	Cor-9BN
HOMO-LUMO gap	7.31	7.71	7.05	7.13	6.95	7.35	8.01	8.94
		Triphenylene	**Phenanthrene**		**Naphthalene**		**Benzene**	
HOMO-LUMO gap		8.46	8.33		8.46		10.54	



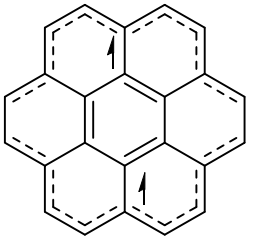
HOMA, EDDB$_P$, NICS(1.7)$_{\pi zz}$-xy scan, AICD

ωB97XD/6-311+G(d,p)

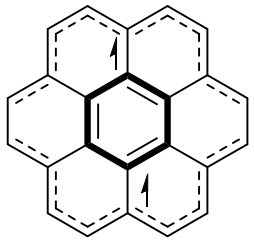
M. Baranac-Stojanović
Unpublished results

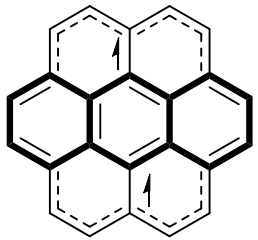


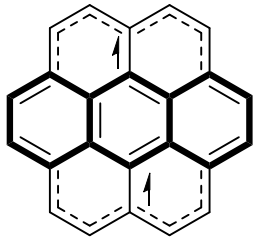
Hirshfeld spin density

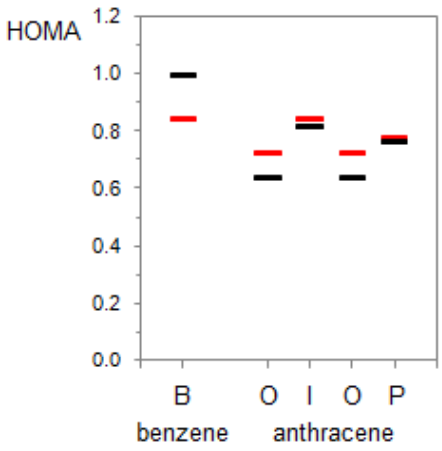


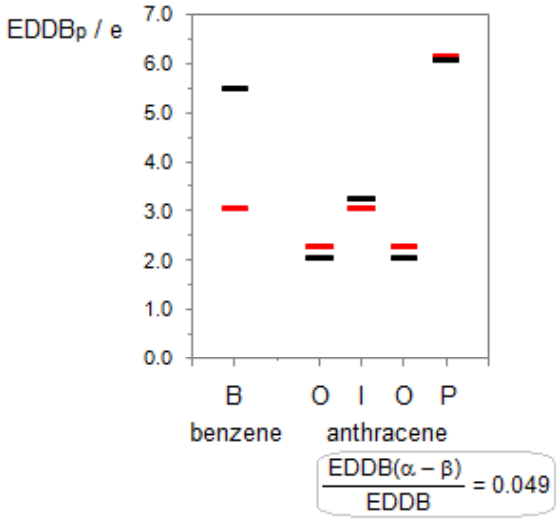
2.8 eV





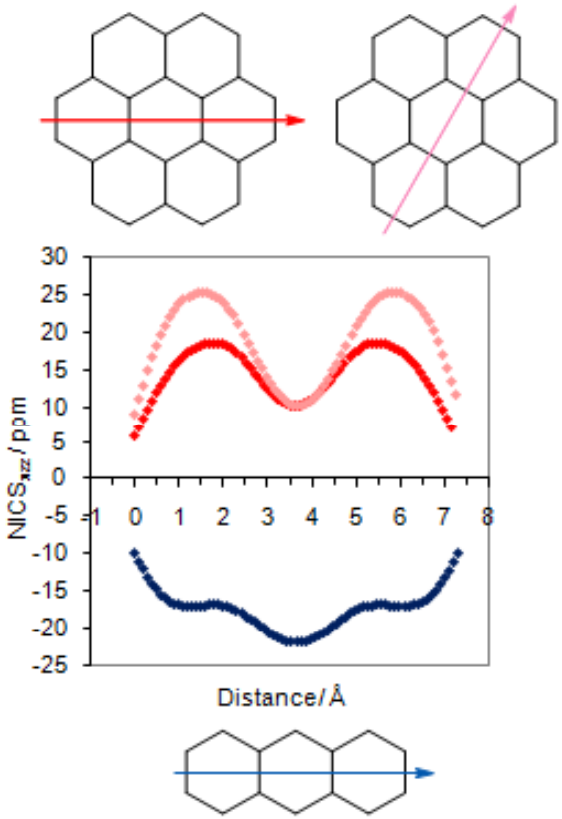


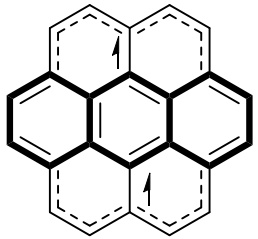


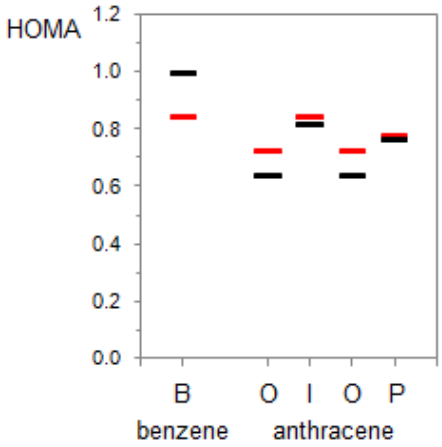


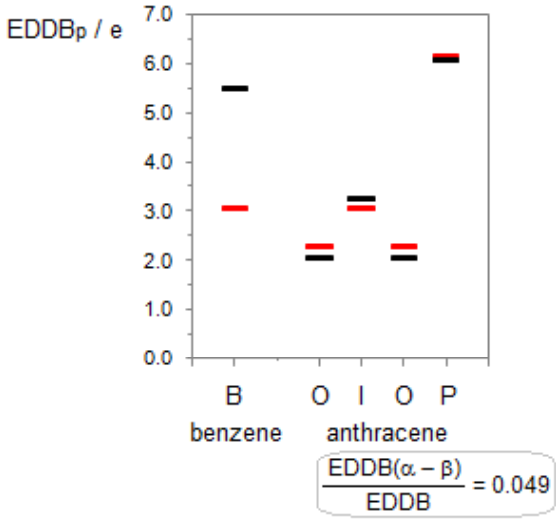
S_0 benzene (B), S_0 anthracene (Outer, Inner, Outer, Perimeter)

Corresponding subunits of T_1 coronene



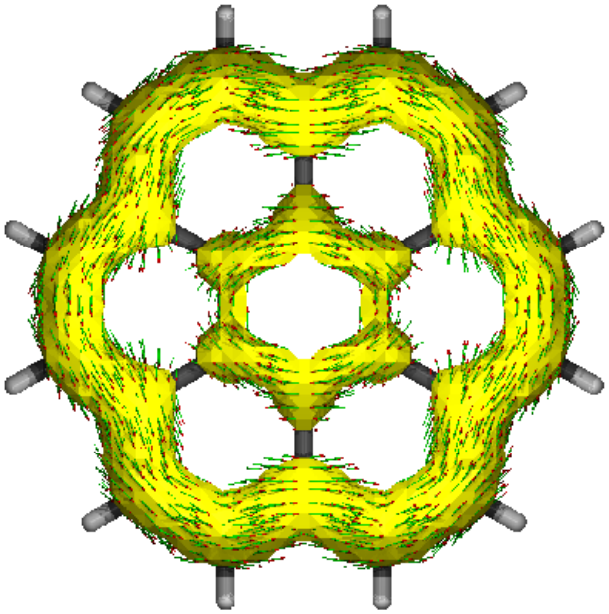






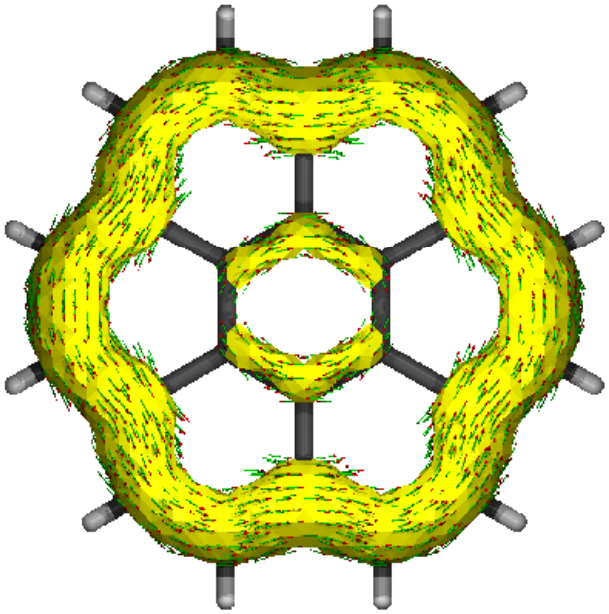
S_0 benzene (B), S_0 anthracene (Outer, Inner, Outer, Perimeter)

Corresponding subunits of T_1 coronene



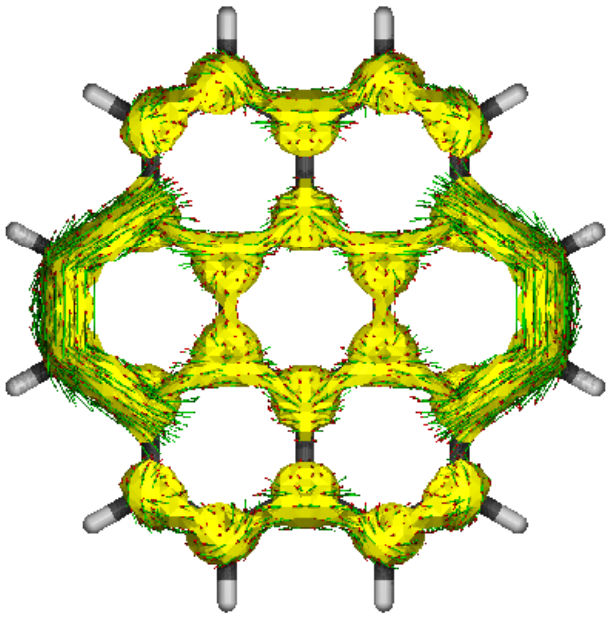
isovalue (a.u.) 0.03

π all



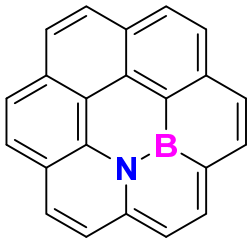
0.03

π unpaired

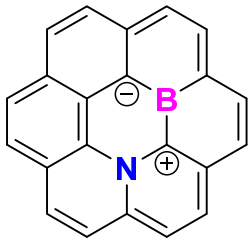


0.02

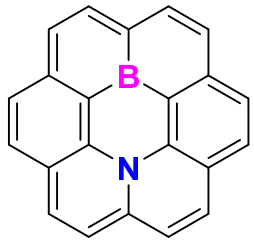
π paired



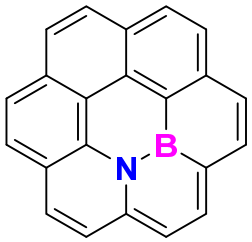
0.0



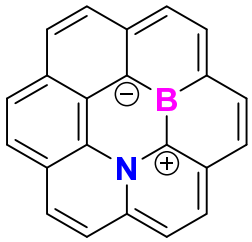
35.1



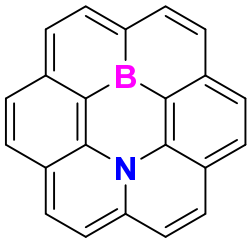
36.8 (kcal/mol)



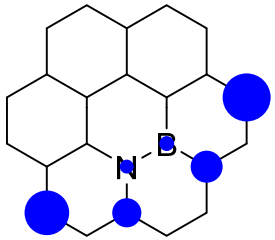
0.0



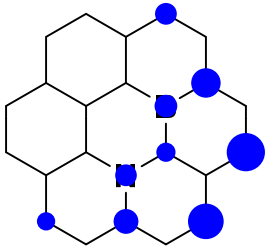
35.1



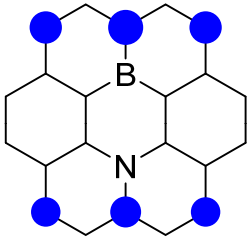
36.8 (kcal/mol)



0.0

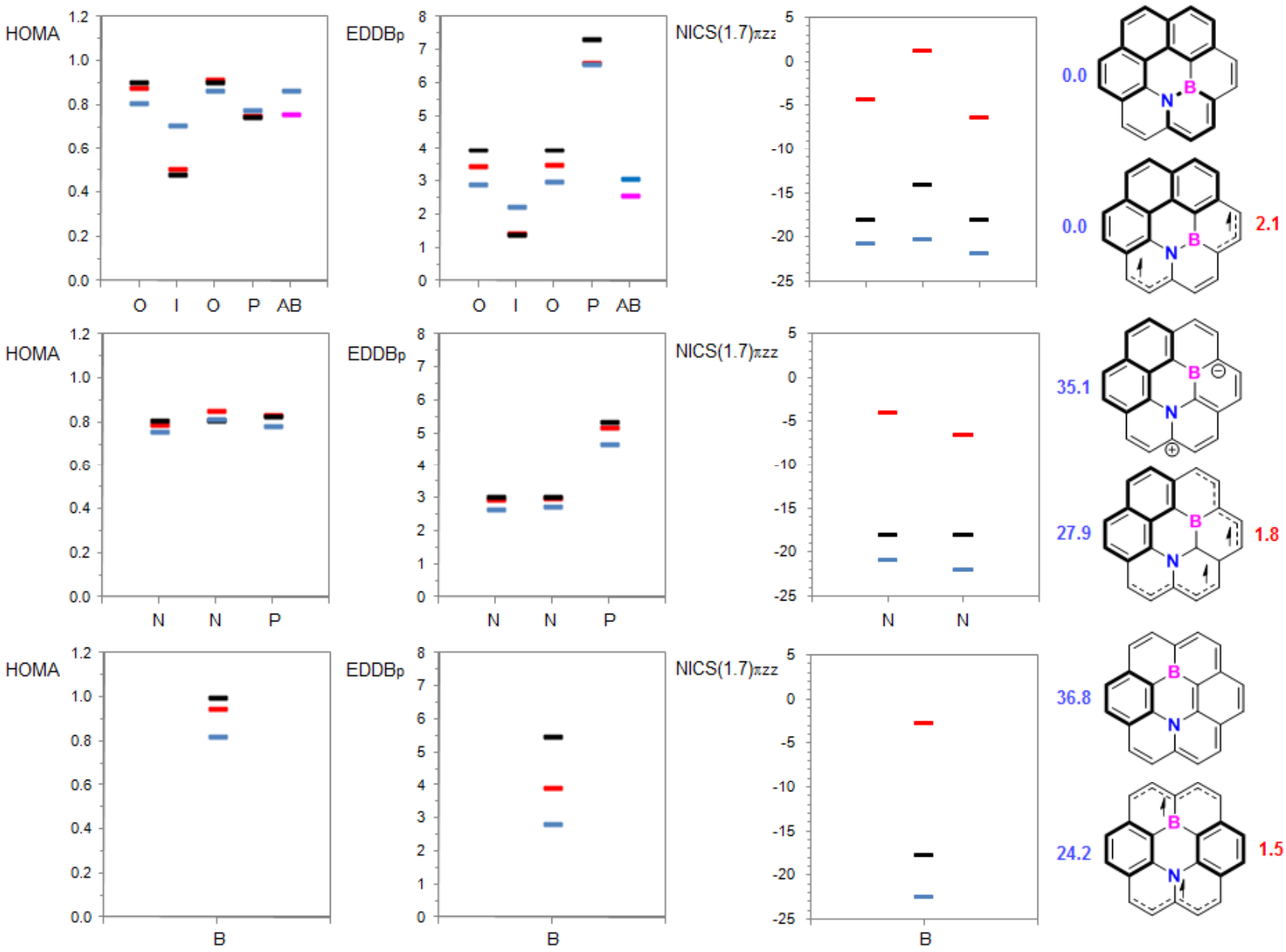


27.9



24.2 (kcal/mol)

Hirshfeld spin density



Isolated hydrocarbon S_0 (Phenanthrene, Naphthalene, Benzene)

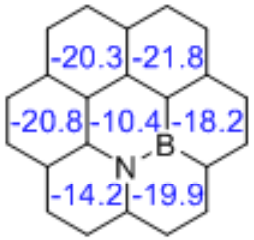
Carbocyclic or BN subunit S_0 **Carbocyclic subunit T_1** **Isolated 1,2-azaborine**

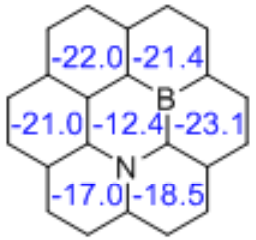
Outer ring of phenanthrene, Inner ring of phenanthrene, Perimeter of molecule
AzaBorine ring, Naphthalene ring, Benzene ring

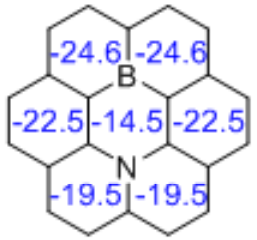
Relative S_0 and T_1 energies (kcal/mol)

S_0-T_1 energy gaps (eV)

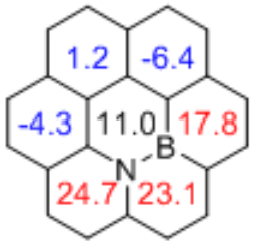
NICS(1.7)π_{zz} S_0

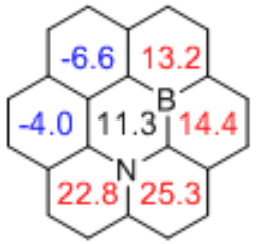


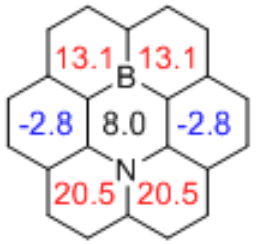




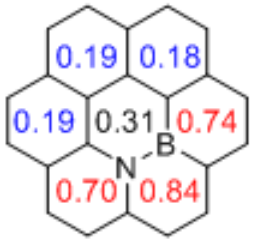
NICS(1.7)π_{zz} T_1

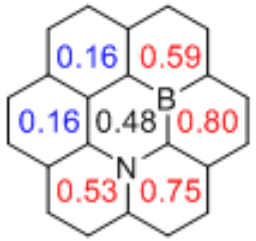


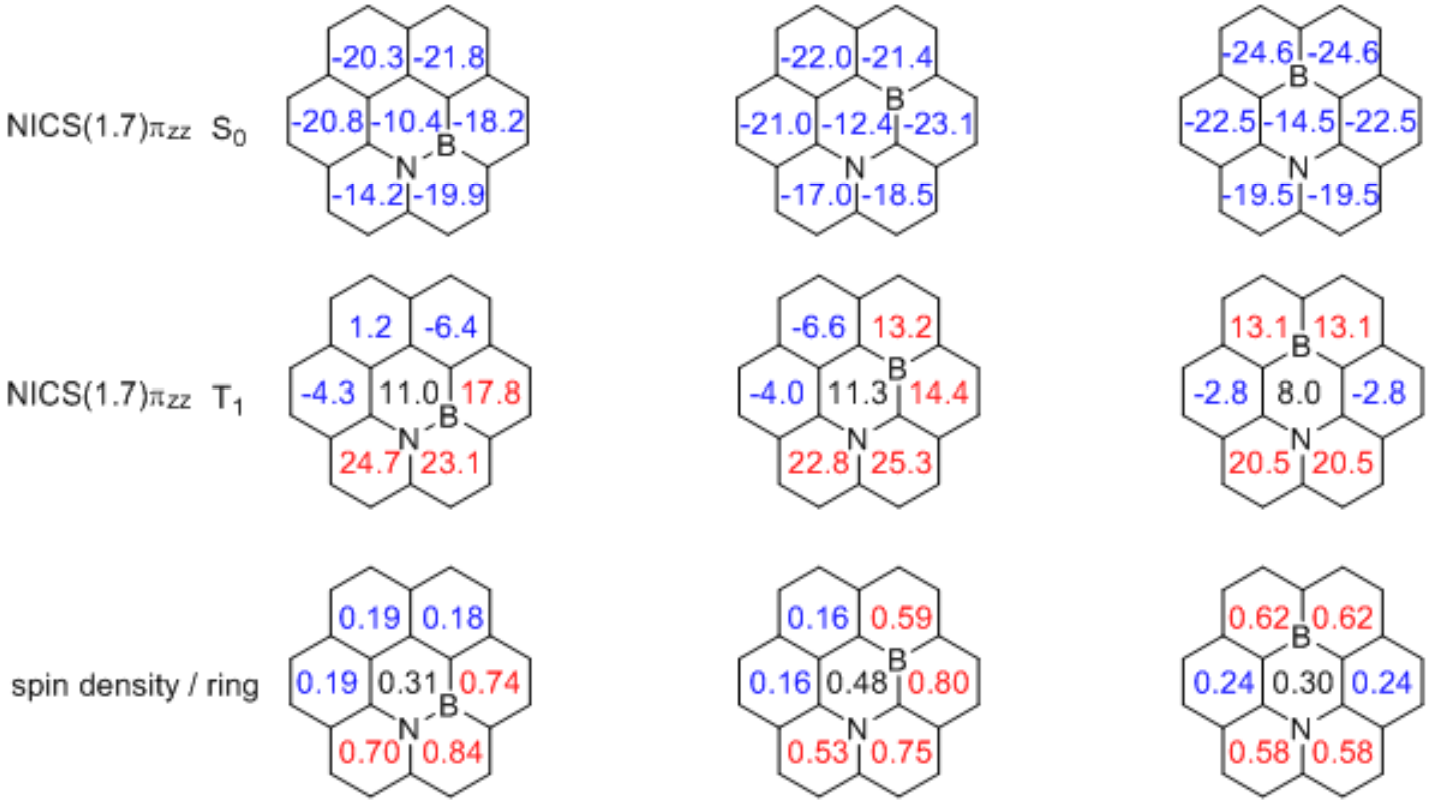




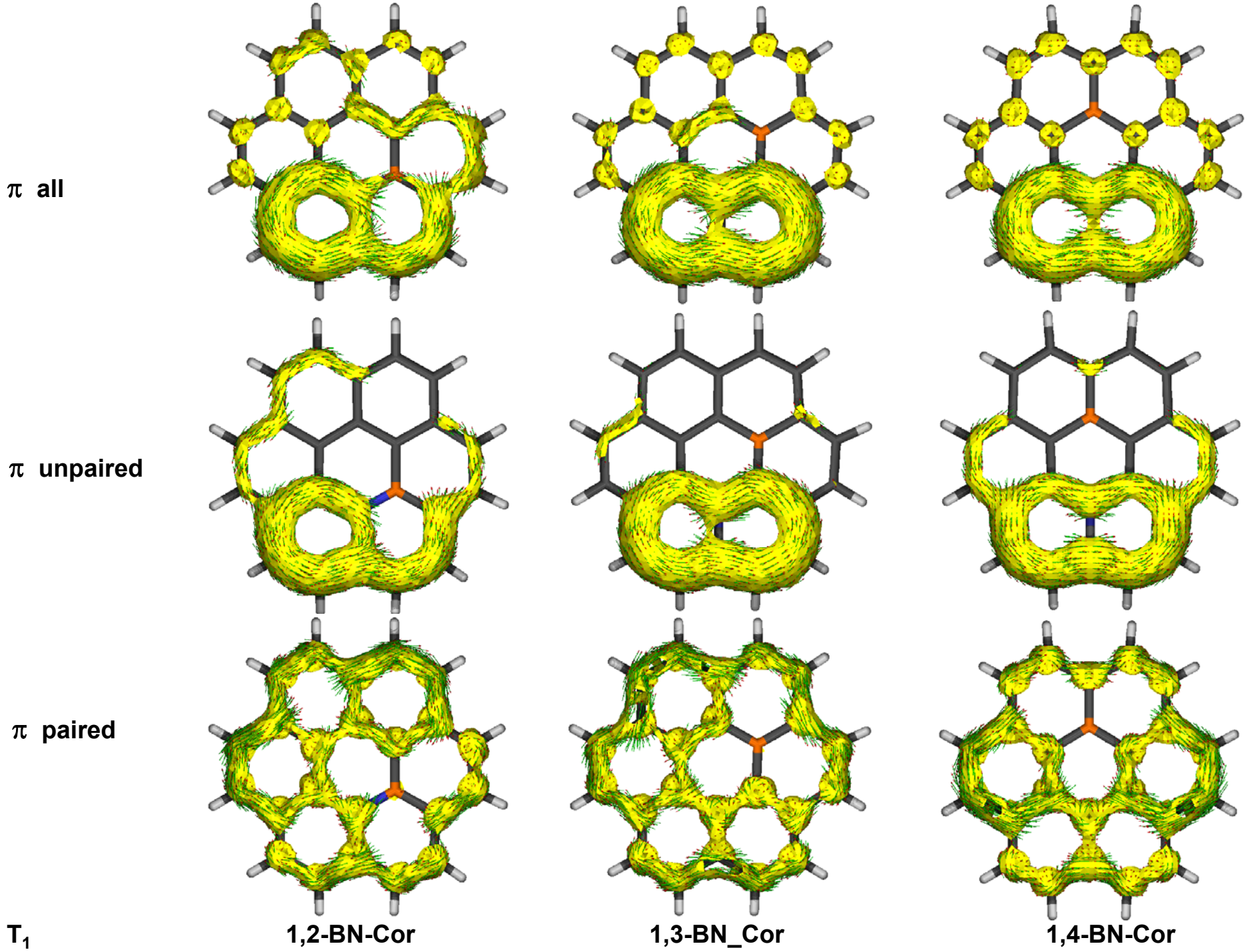
spin density / ring

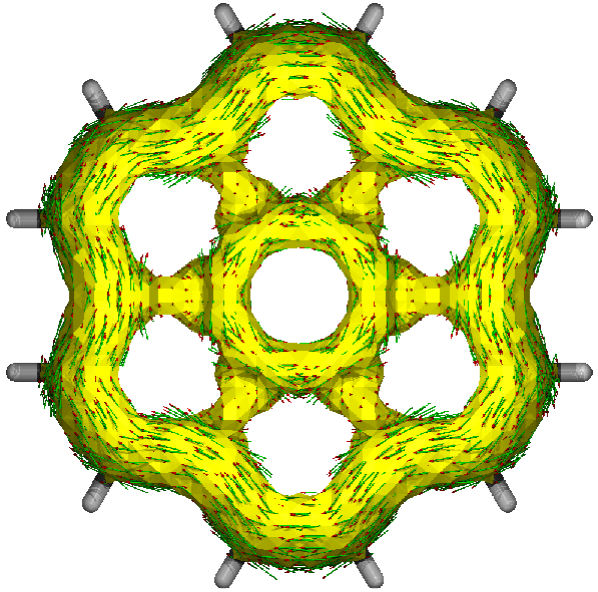




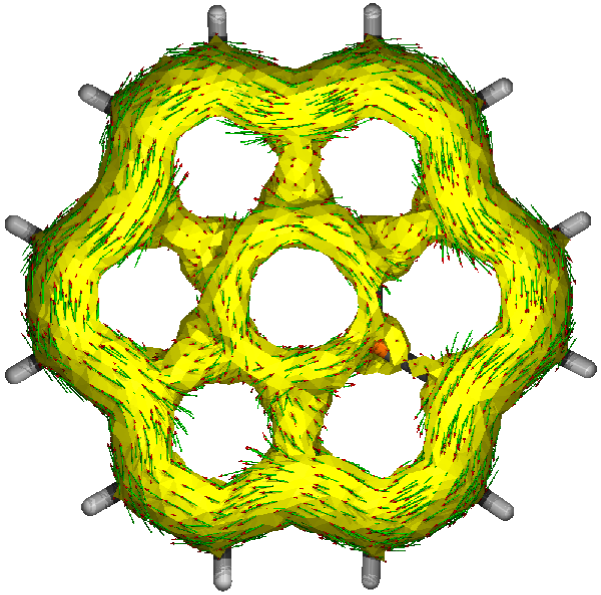


G. Markert, E. Paenurk, R. Gershoni-Poranne, CEJ 2021, *27*, 6923.

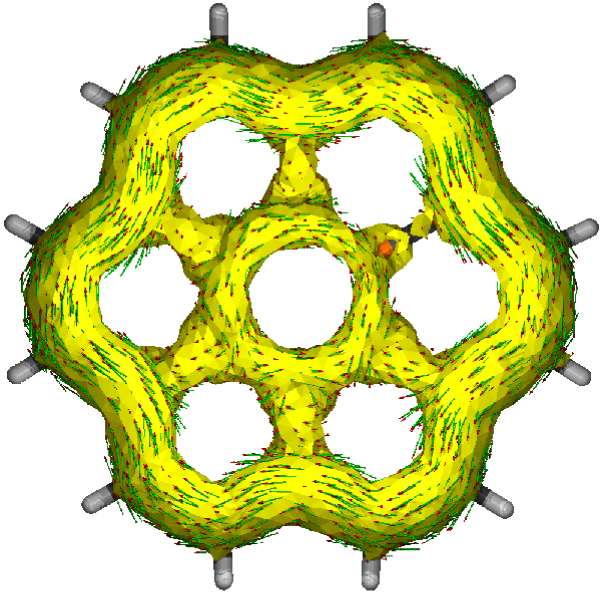

π all
π unpaired
π paired
T1
1,2-BN-Cor
1,3-BN_Cor
1,4-BN-Cor



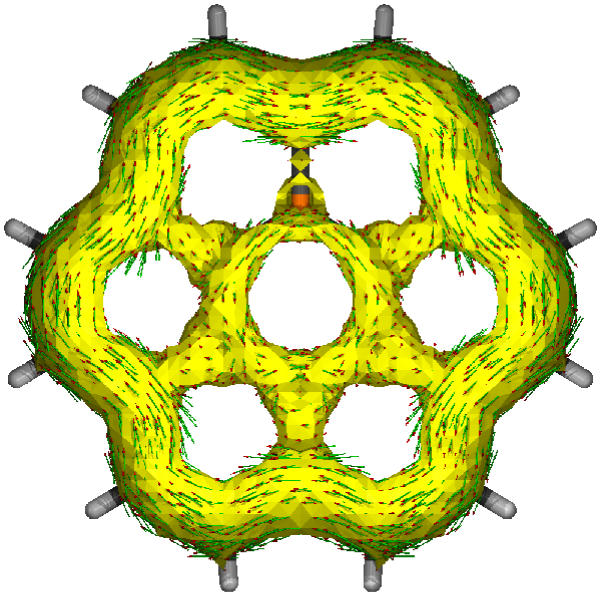
Cor



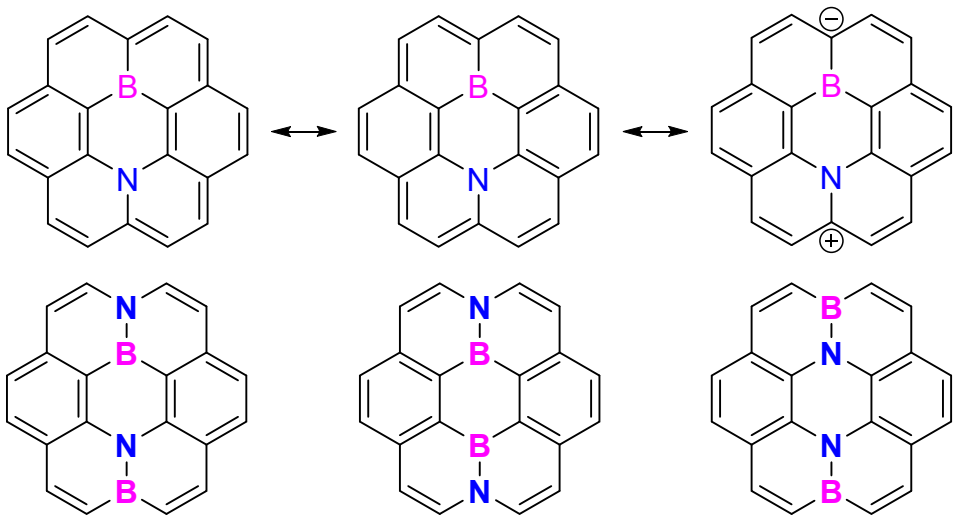
S_0 1,2-BN-Cor

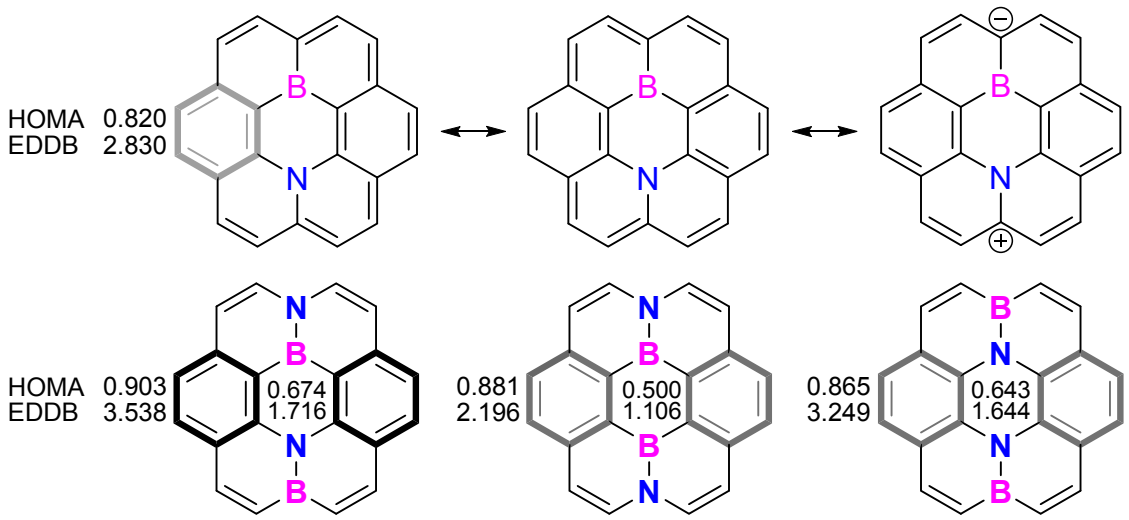


1,3-BN-Cor



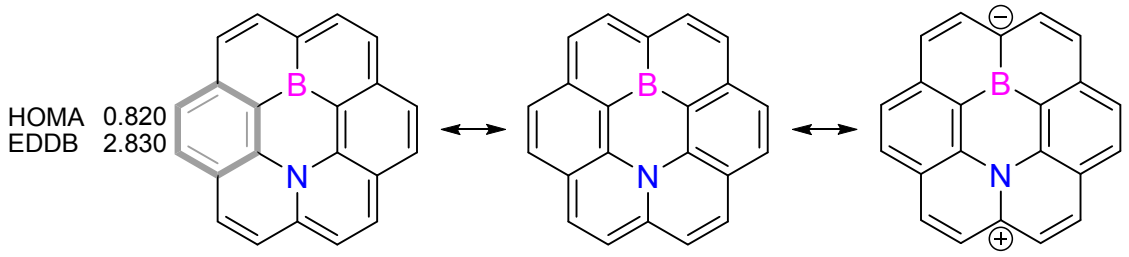
1,4-BN-Cor

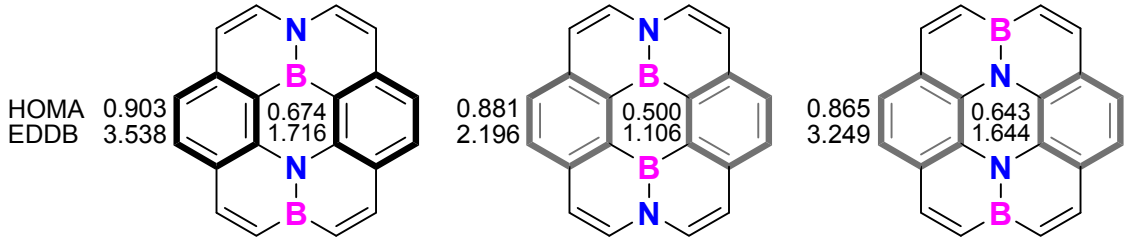

B
N
B
N
B
N
N
B
N
B
N
B
N
B
B
N
N
B



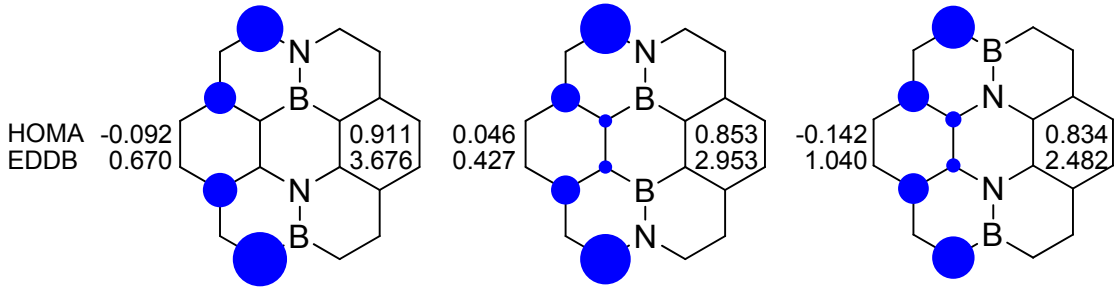
relative energy (kcal/mol)

0.0 5.4 3.2



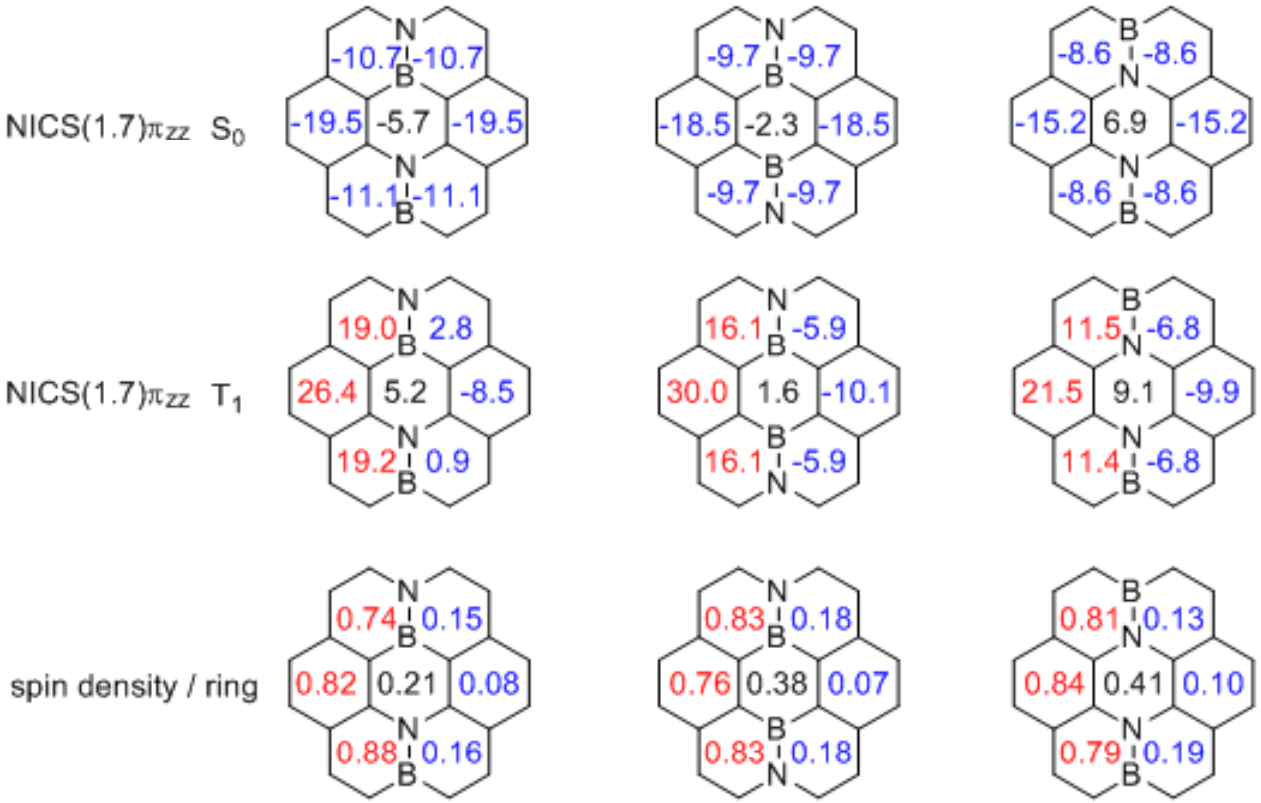


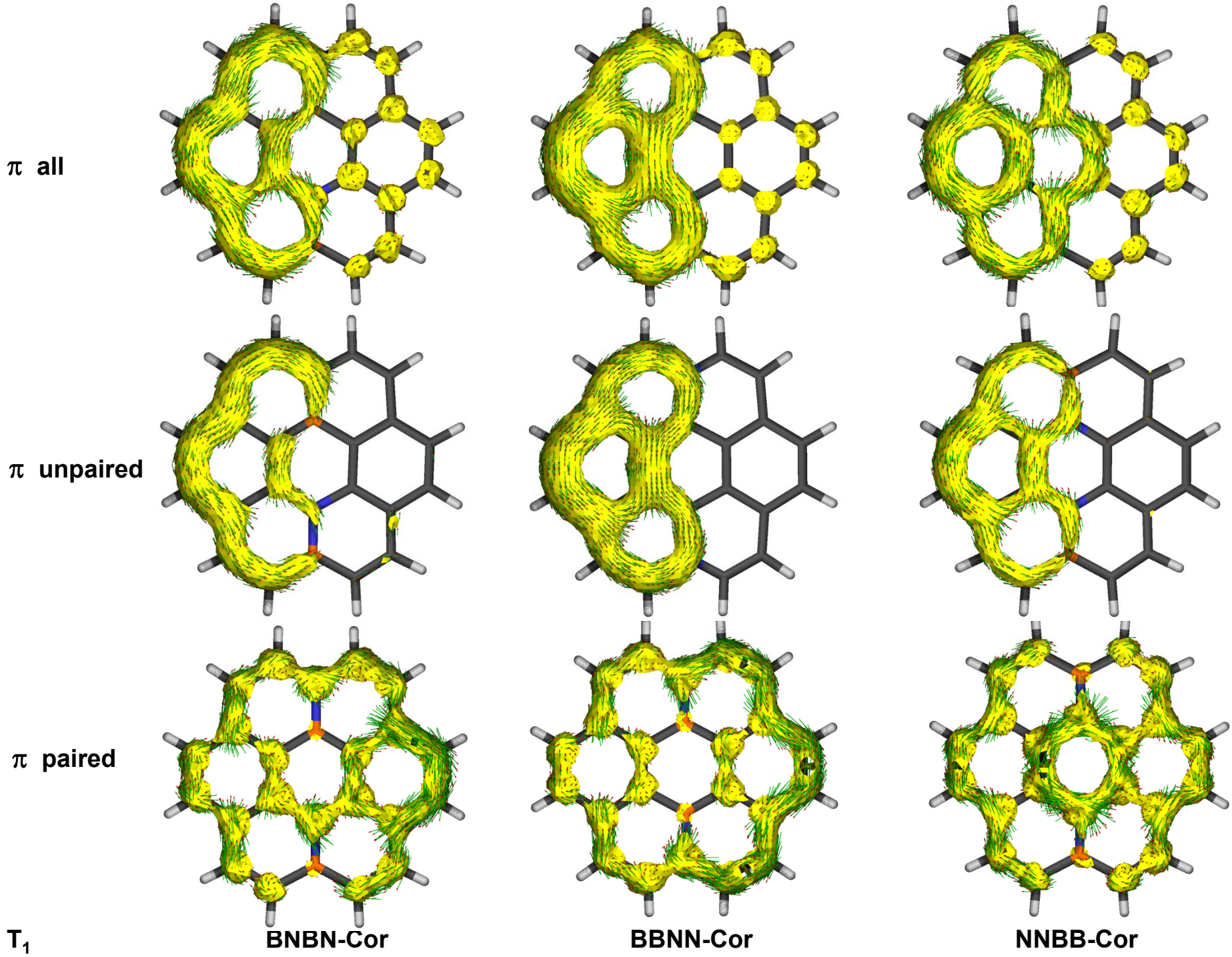
relative energy (kcal/mol) 0.0 5.4 3.2

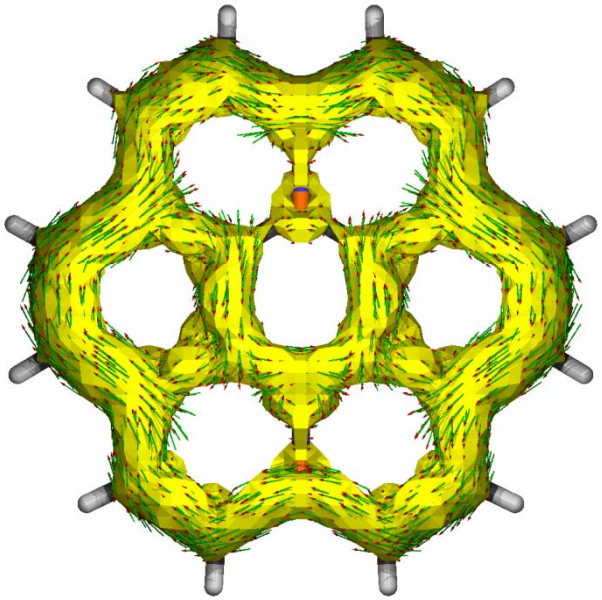


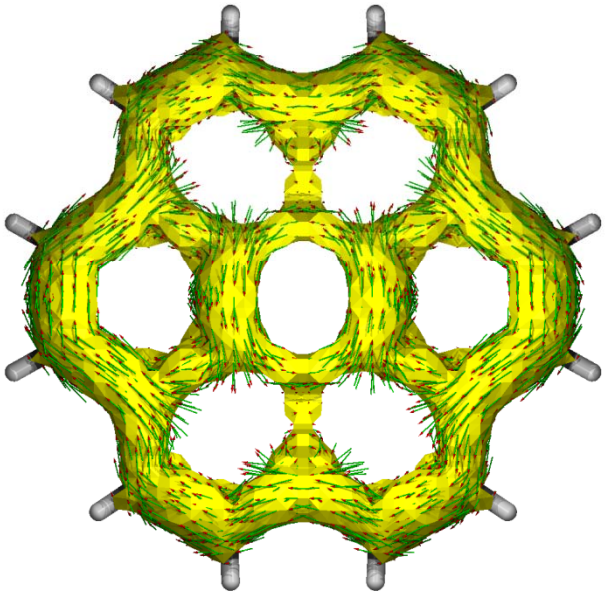
relative energy (kcal/mol) 0.0 6.4 4.3

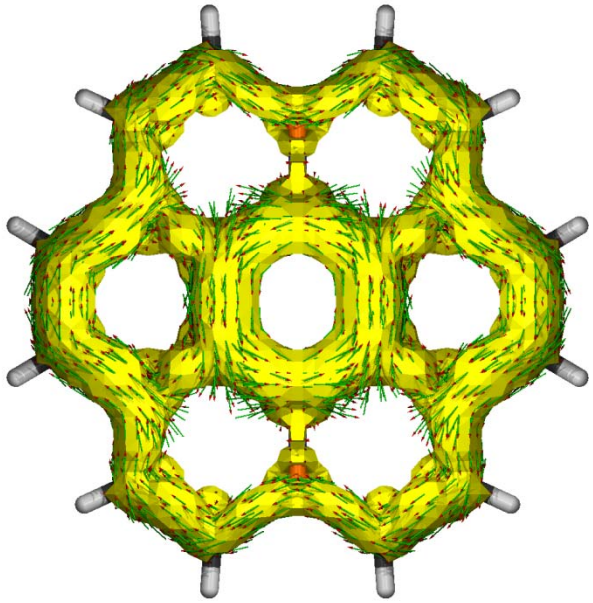
S_0-T_1 (eV) 2.8 2.8 2.8


NICS(1.7)πzz S0
-10.7 -10.7
-19.5 -5.7 -19.5
-11.1 -11.1
-9.7 -9.7
-18.5 -2.3 -18.5
-9.7 -9.7
-8.6 -8.6
-15.2 6.9 -15.2
-8.6 -8.6
NICS(1.7)πzz T1
19.0 2.8
26.4 5.2 -8.5
19.2 0.9
16.1 -5.9
30.0 1.6 -10.1
16.1 -5.9
11.5 -6.8
21.5 9.1 -9.9
11.4 -6.8
spin density / ring
0.74 0.15
0.82 0.21 0.08
0.88 0.16
0.83 0.18
0.76 0.38 0.07
0.83 0.18
0.81 0.13
0.84 0.41 0.10
0.79 0.19

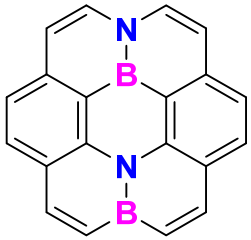

π all
π unpaired
π paired
T1
BNBN-Cor
BBNN-Cor
NNBB-Cor

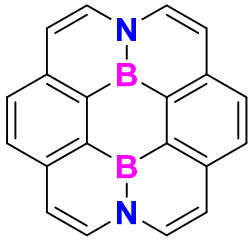


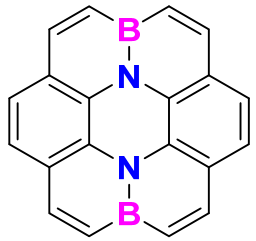




S_0 **BNBN-Cor** **BBNN-Cor** **NNBB-Cor**







Conclusions

There is a tendency towards the formation of aromatic hydrocarbon subunits in polycyclic compounds.

This can affect HOMO-LUMO energy gap, spin density distribution in T_1 state and S_0-T_1 energy gap.

Acknowledgement

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Dr. Milovan Stojanović, ICTM-Center for Chemistry, University of Belgrade

Dr. Jovana Aleksić, ICTM-Center for Chemistry, University of Belgrade

Thank you for your attention!