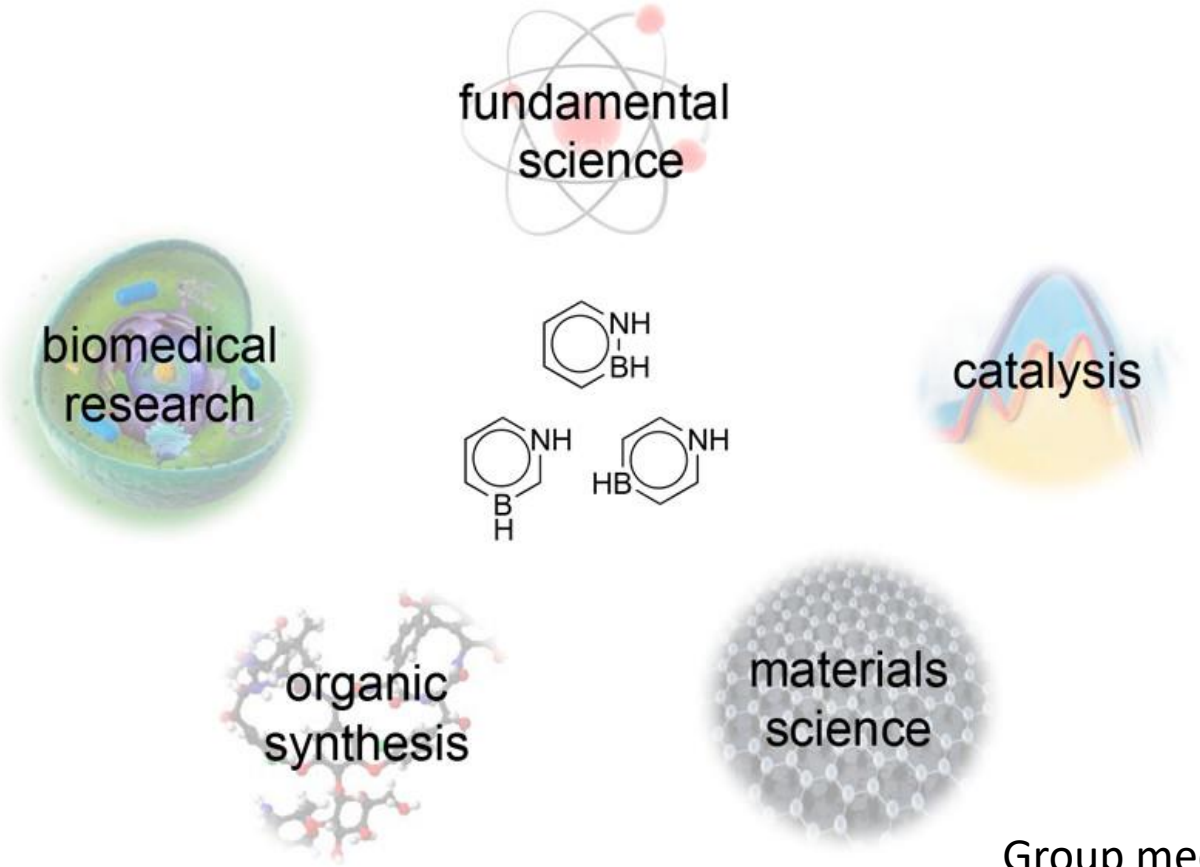
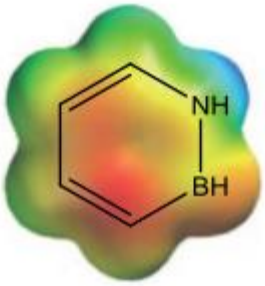
Fundamental Research on Probing the Stability of BN-doped Pentalenes



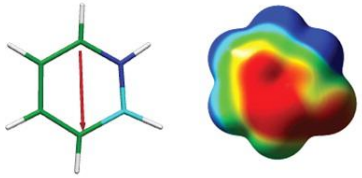
Danling Zhuang
Advisor: Jun Zhu
Group meeting @2018.09.30

Content



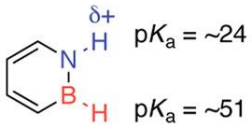
- Introduction
- Motivation
- Computational details
- Discussion and results
- Question

Isoelectronic Relationship



Dipole Moment: ~2.2 D

pK_a (B3LYP/DZVP2) values in H_2O (ref 15)

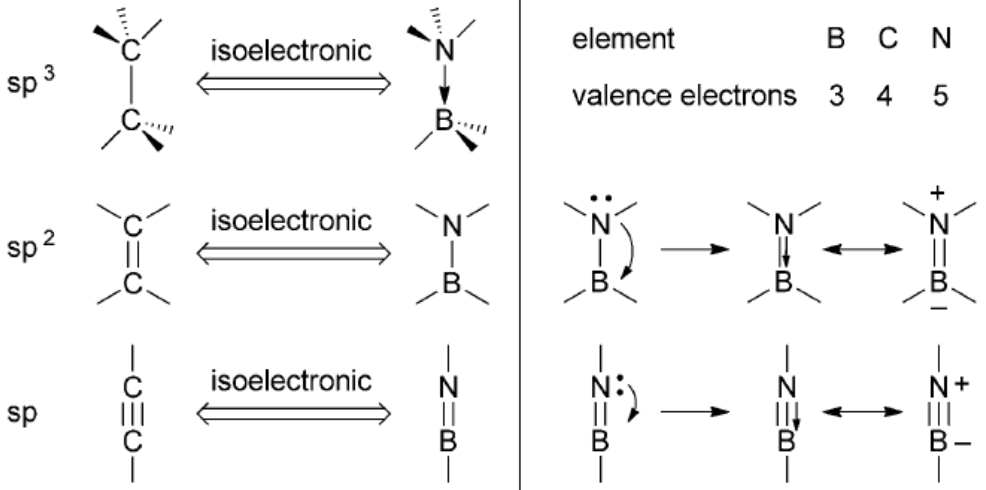


Ab

vs.

benzene

N-H hydrogen bonding



BDE (CC, covalent): 90.1 kcal mol^{-1}

μ = 0 Debye

ethane

ammonia borane

BDE (BN, dative): 27.2 kcal mol^{-1}

μ = 5.216 Debye

BDE (CC): 174.1 kcal mol^{-1} (109.1 kcal mol^{-1} σ, 65 kcal mol^{-1} π)

μ = 0 Debye

ethene

aminoborane

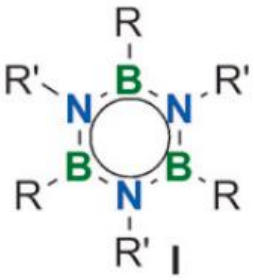
BDE (BN): 139.7 kcal mol^{-1} (109.8 kcal mol^{-1} σ, 29.9 kcal mol^{-1} π)

μ = 1.844 Debye

Liu, S.-Y. et. al. *Angew. Chem. Int. Ed.* **2012**, *51*, 6074-6092

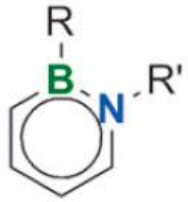
The history of BN-aromatics

Stock

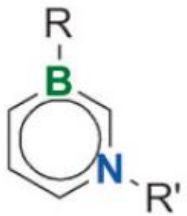


Borazine
1926

Dewar

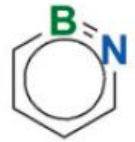


II
Dewar
1962

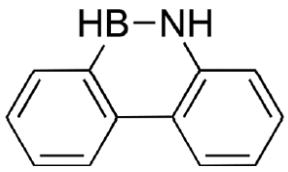


III
Liu
2011

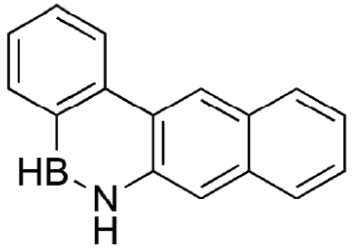
IV
Braunschweig
2012



V
Bettinger
2015



Dewar 1958

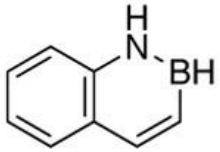
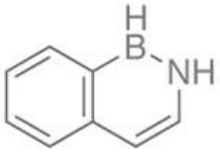
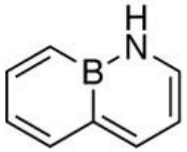
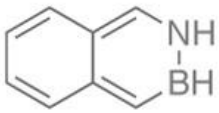
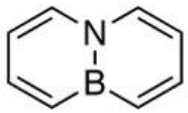
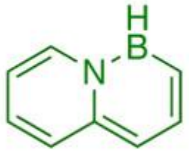


Dewar 1963

Z. X. Giustra and S. Y. Liu, *J Am Chem Soc*, 2018, **140**, 1184.
H. Helten, *Chem Eur J*, 2016, **22**, 12972.

orientational isosteres

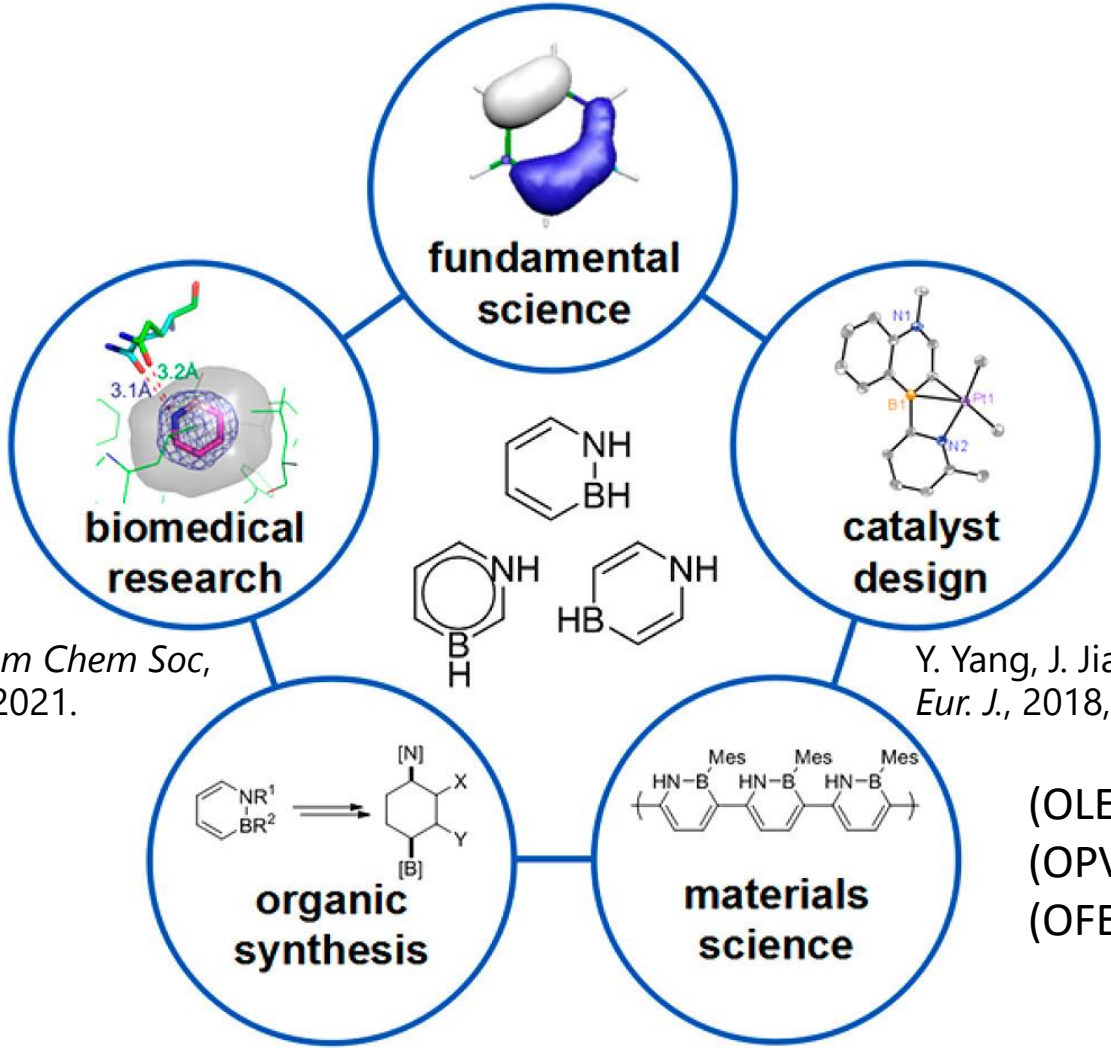
BN naphthalene series:

Dewar (1959)		Liu (2015)		Dewar (1964)	this work
					
BN-1,2-Naph	BN-2,1-Naph	**BN-1,9-Naph**	BN-2,3-Naph	BN-9,10-Naph	**BN-9,1-Naph**
ΔH_f: 12.6	13.0	21.7	23.8	25.5	31.3

most thermodynamically stable ⟶ least thermodynamically stable

Shih-Yuan Liu

The scope of BN-aromatics



Liu. *et al* , *J Am Chem Soc*, 2016, **138**, 12021.

Y. Yang, J. Jiang, H. Yu and J. Shi, *Chem. Eur. J.*, 2018, **24**, 178.

(OLEDs)
(OPVs)
(OFETs)

Liu . *et al*, *ACS Nano*, 2017, **11**, 2486.

Z. X. Giustra and S. Y. Liu, *J Am Chem Soc*, 2018, **140**, 1184.

Shih-yuan liu and his azaborine family

Position: Professor of Chemistry, **Boston College**, Chestnut Hill, Massachusetts (USA)

Education:

1994–1997 Diplom (awarded in 1998), Vienna University of Technology

1997–1998 Exchange student, University of North Carolina at Chapel Hill

1998–2003 PhD with Gregory C. Fu, Massachusetts Institute of Technology (MIT)

2003–2006 Postdoctoral associate with Daniel G. Nocera, MIT

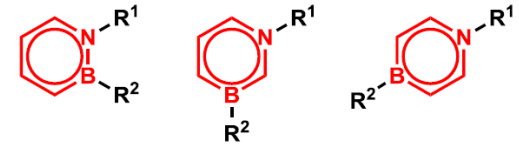
Shih-Yuan Liu

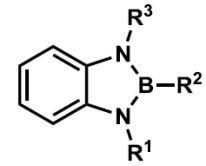
Awards:

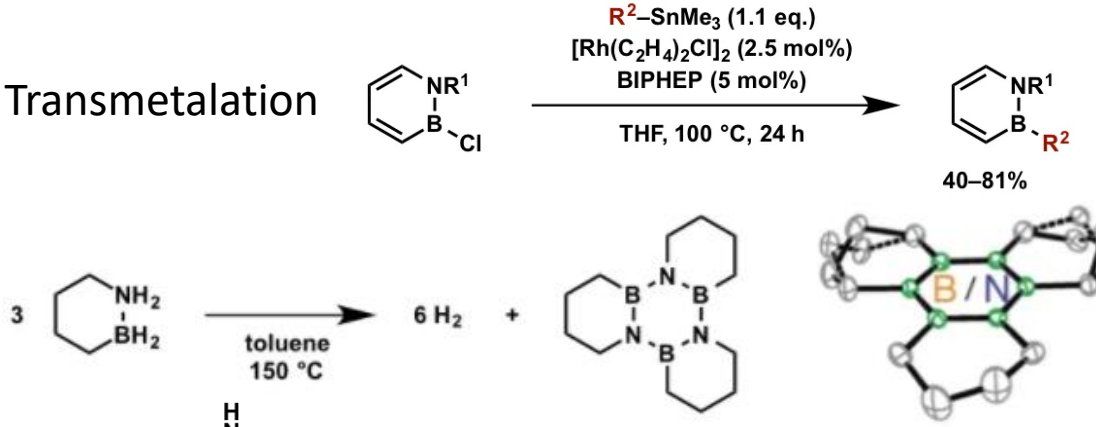
2012 Journal of Physical Organic Chemistry Award for Early Excellence;

2012 Camille Dreyfus; Teacher-Scholar Award; 2014 Organometallics Young Investigator Fellow

Current research interests: Synthetic organic/organometallic chemistry, **basic science of BN/CC isosterism**, **BN heterocycles**, hydrogen-storage materials, boron-containing pharmacophores

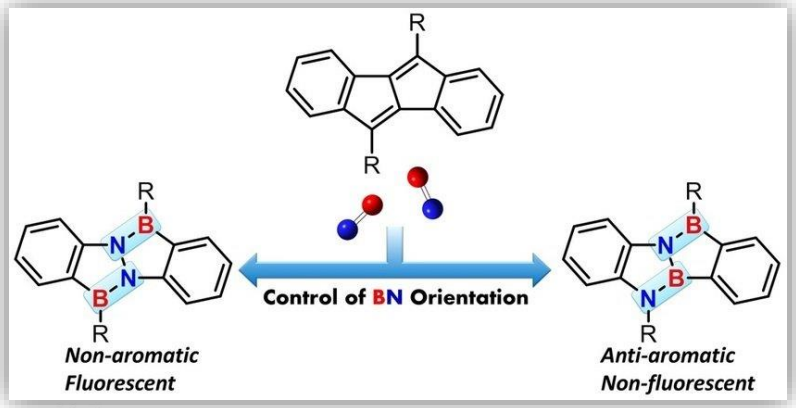


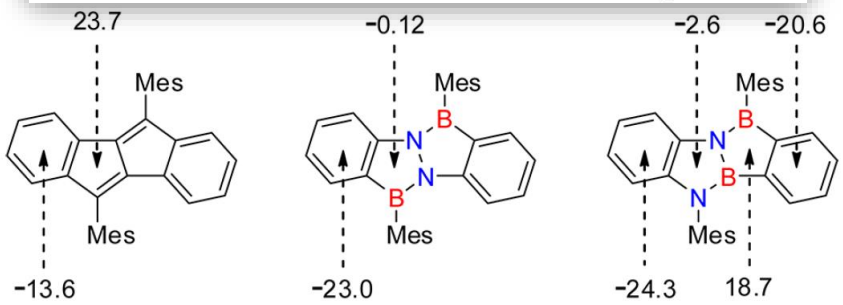




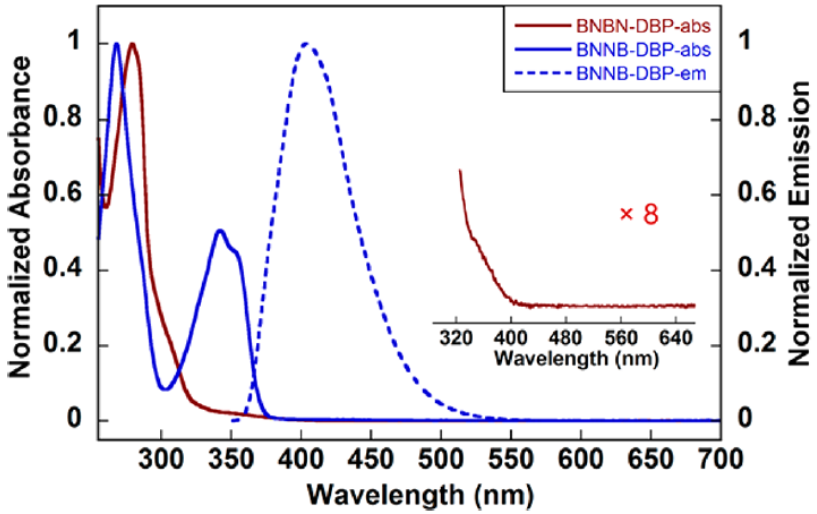
Author profile, *Angew Chem Int Ed*, **2015**, *54*, 726.

B_2N_2-Dibenzo[a,e]pentalenes



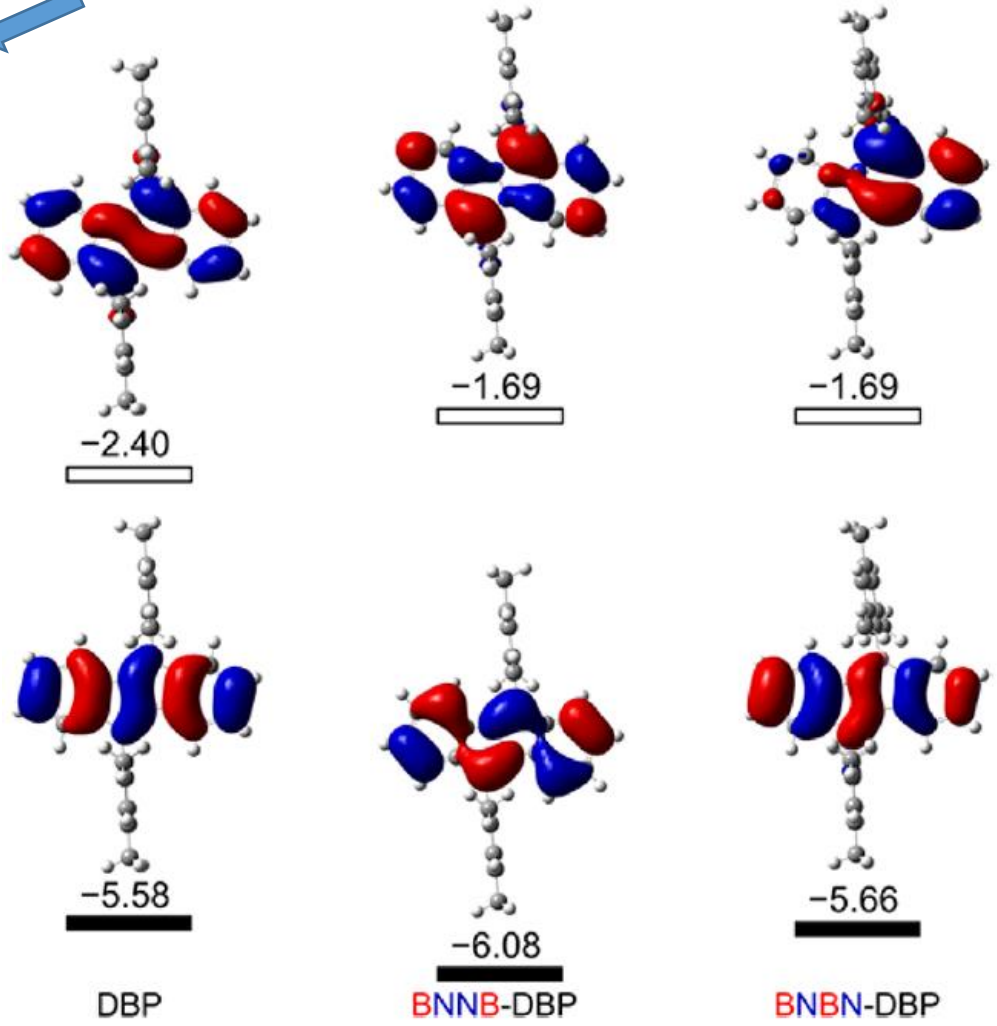


Antiaromaticity



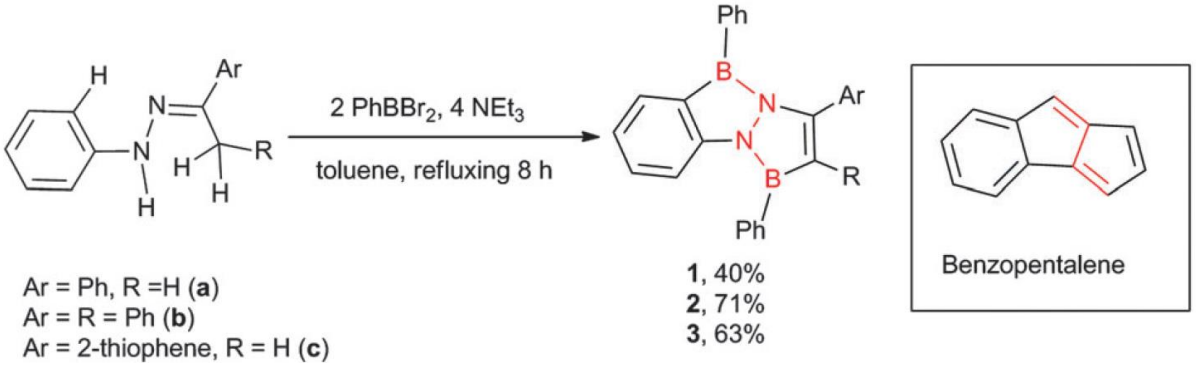
Optoelectronic Properties

BN Orientation Pattern

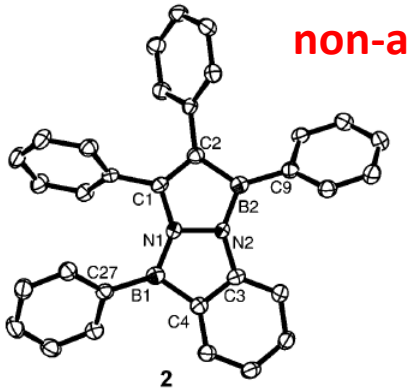


X. Y. Wang, A. Narita, X. Feng and K. Mullen, *J Am Chem Soc*, 2015, **137**, 7668.

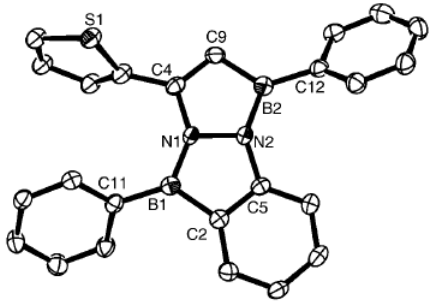
Boron–nitrogen analogues of benzopentalene



non-aromatic



2



3

- larger HOMO–LUMO gaps
- higher energy absorption
- higher emission maxima
- Non-aromatic rather than anti-aromatic

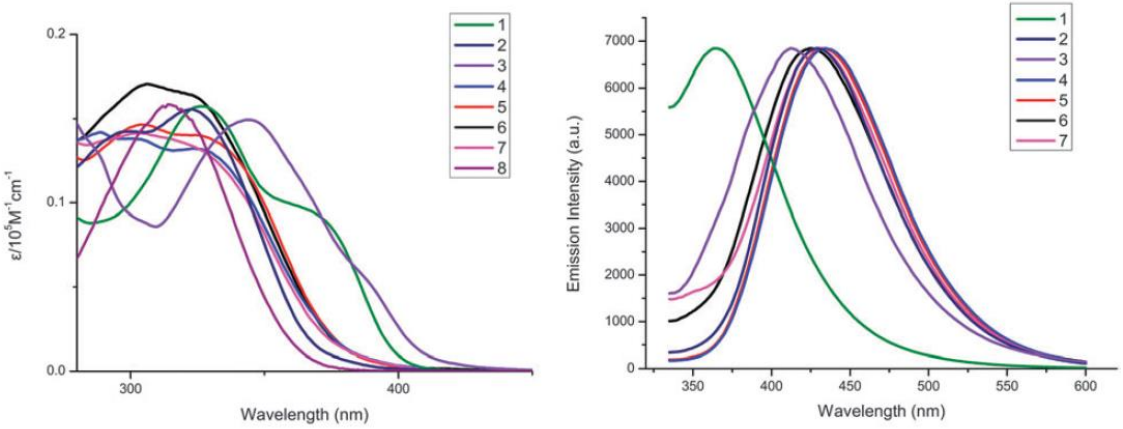
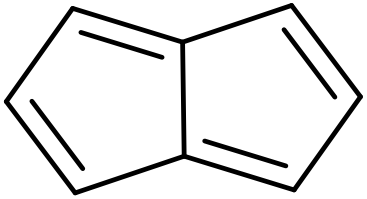


Fig. 2 UV-vis (left) and emission (right) spectra of **1–7** in *n*-hexane.

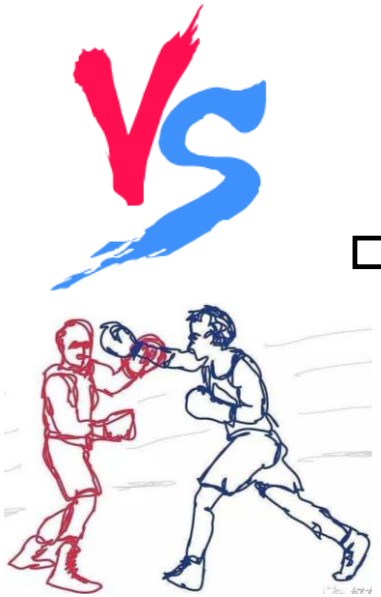
C. Ma, J. Zhang, J. Li and C. Cui, *Chem Commun*, 2015, **51**, 5732.

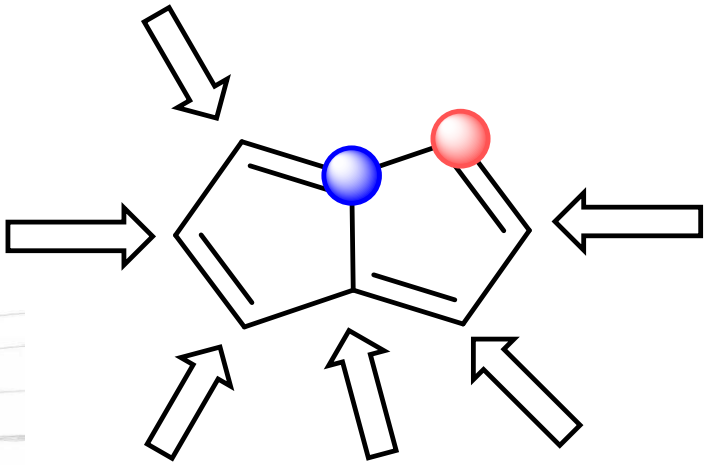
Motivation

Anti-aromatics



Pentalene





BN-Pentalenes

- Which isomer of BN-pentalene is most stable one?
- Which factor causes the stability? Aromaticity? Or ?

??

Electrostatic potentials
Dipole moment
Bond order
Charge distribution
Ring strain
……

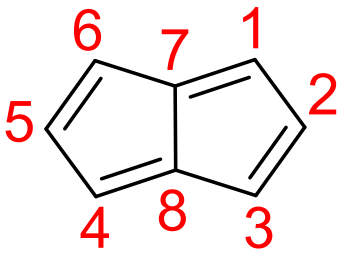
Computational details

Gaussian 16 A.03

Optimization M06-2X/def2-TZVP

Single point CCSD(T)/def2-TZVP

Numbering method



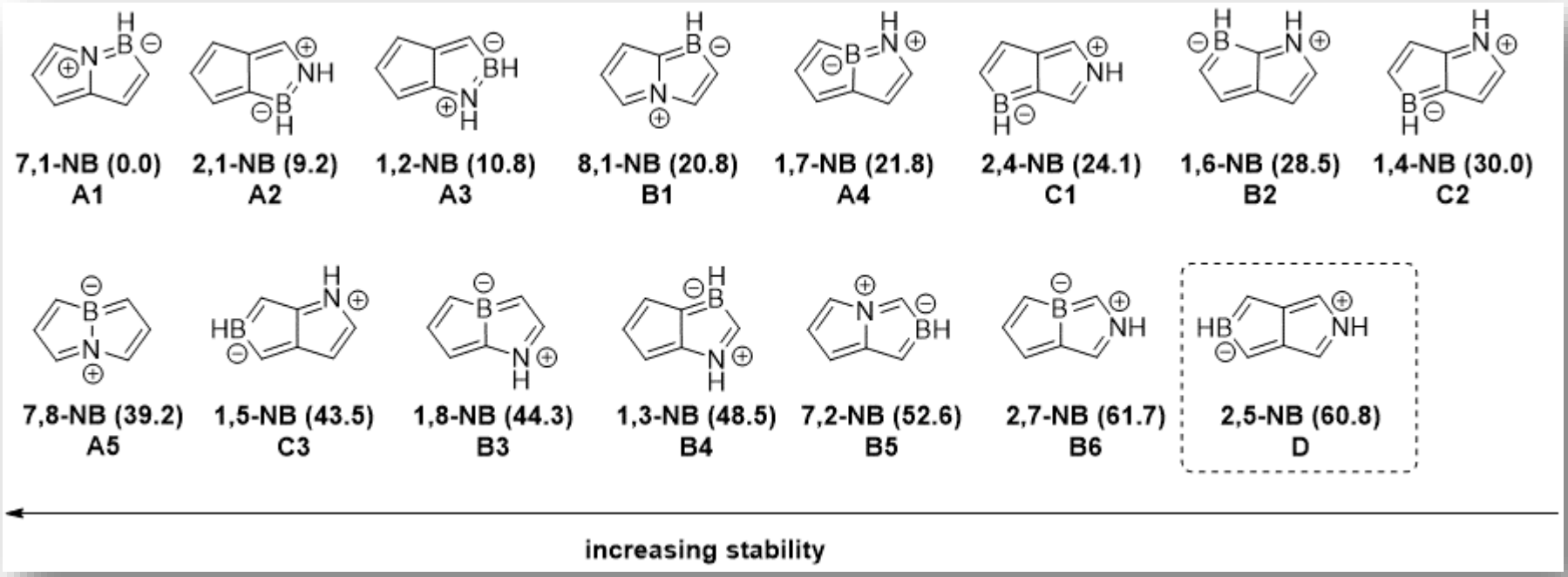
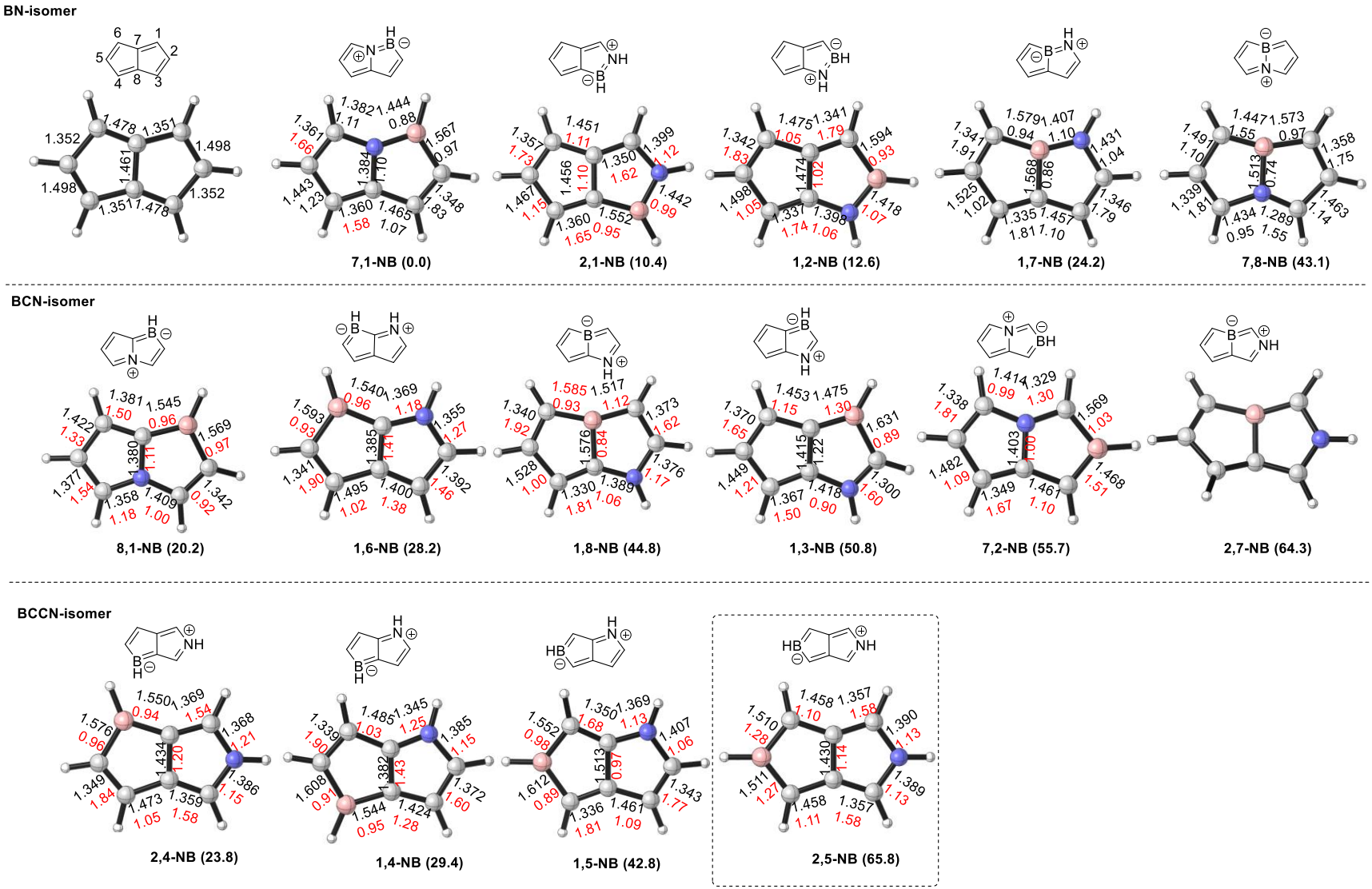
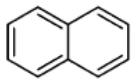
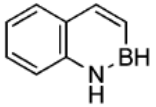
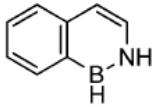
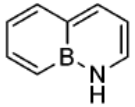
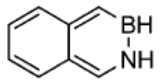
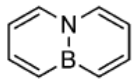
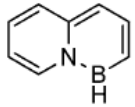


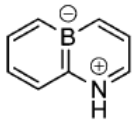
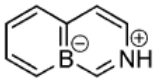
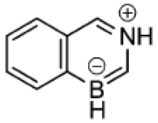
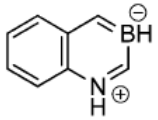
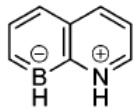
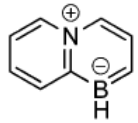
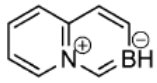
Figure 1. Big picture for the trend of stability of all isomers we investigated. Electronic energies are given in kcal/mol.

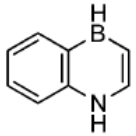
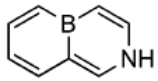
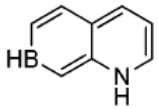
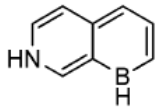
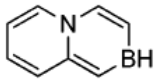
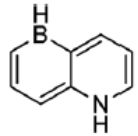
Bond lengths and Wiberg bond order

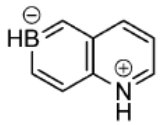
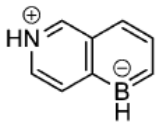
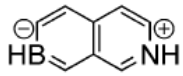
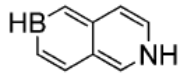


BN-doped simplest ring-fused aromatics

Compound							
							
Isomer		1,2	2,1	1,10	2,3	5,10	10,1
E_{rel}		0.00	0.40	7.87	10.68	12.85	17.96

Compound							
							
Isomer	1,5	2,10	3,1	1,3	1,9	5,1	10,2
E_{rel}	0.00	1.46	1.53	2.00	8.58	10.37	11.54
E_{rel}^{b}	32.43	33.88	33.96	34.43	41.01	42.80	43.97

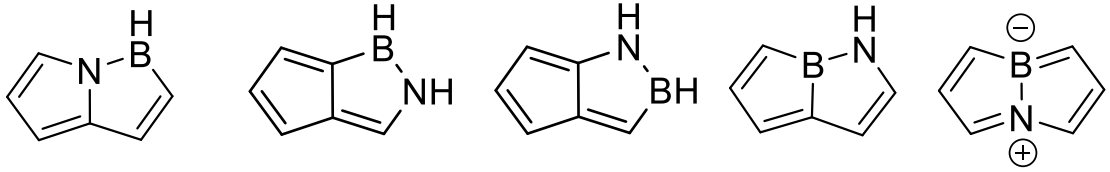
Compound						
						
Isomer	1,4	2,5	1,8	8,1	5,2	1,6
E_{rel}	0.00	7.35	15.97	17.07	17.85	18.09
E_{rel}^{b}	22.61	29.96	38.59	39.69	40.46	40.71

Compound					
					
Isomer	1,7	7,1	2,8	2,7	
E_{rel}	0.00	0.88	1.44	0.00	
E_{rel}^{b}	46.56	47.44	48.00	41.72	

M. Stojanović and M. Baranac-Stojanović, *New. J. Chem.*, 2018, **42**, 12968.

Different Catalogs of BN-pentalenes

1,2-series

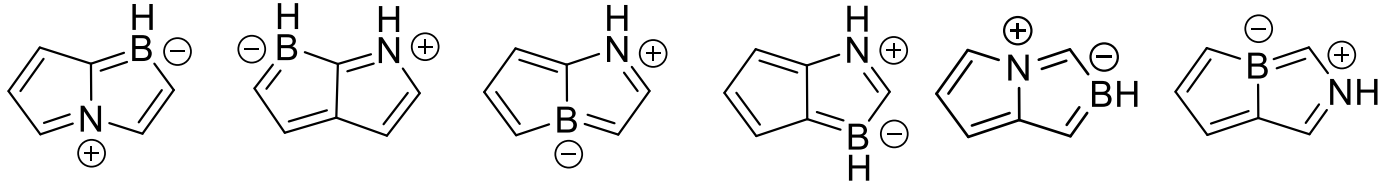


7,1	2,1	1,2	1,7	7,8
0	9.2	10.8	21.8	39.2

$\Delta E_{CCSD(T)}$ (kcal/mol)

Increasing Stability

1,3-series

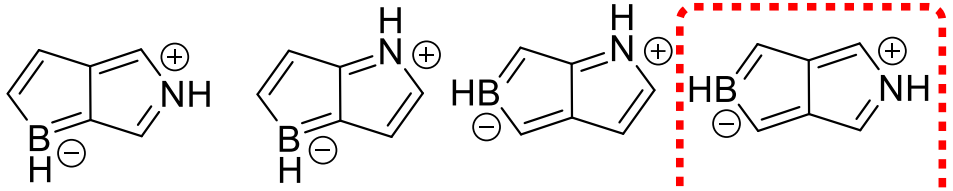


8,1	1,6	1,8	1,3	7,2	2,7
20.8	28.5	44.3	48.5	52.6	61.7

$\Delta E_{CCSD(T)}$ (kcal/mol)

Increasing Stability

1,4-series



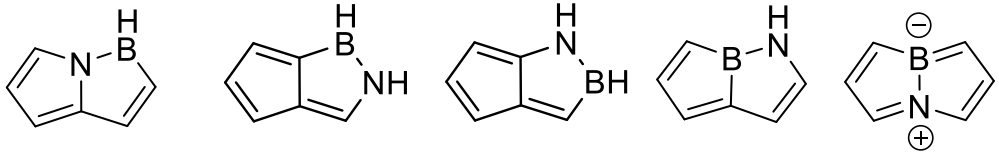
2,4	1,4	1,5	2,5
24.1	30.0	43.5	60.8

$\Delta E_{CCSD(T)}$ (kcal/mol)

Increasing Stability

HOMO-LUMO Gap

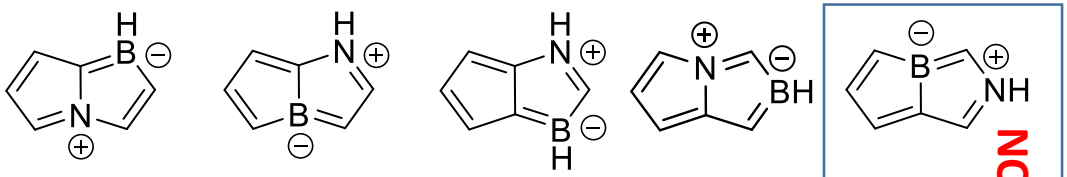
1,2-series



	7,1	2,1	1,2	1,7	7,8
$\Delta E_{CCSD(T)}$ (kcal/mol)	0	9.2	10.8	21.8	39.2
$\Delta E_{LUMO-HOMO}$ (a. u.)	5.68	6.53	5.33	5.22	3.89

Increasing Stability

1,3-series

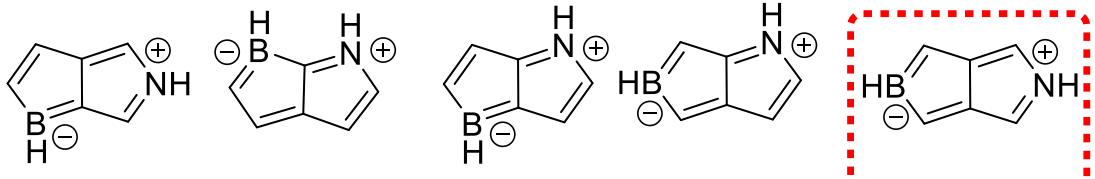


	8,1	1,8	1,3	7,2	2,7
$\Delta E_{CCSD(T)}$ (kcal/mol)	20.8	44.3	48.5	52.6	61.7
$\Delta E_{LUMO-HOMO}$ (a. u.)	5.78	5.04	4.44	3.78	4.42

NON-PLANAR

Increasing Stability

1,4-series



	2,4	1,6	1,4	1,5	2,5
$\Delta E_{CCSD(T)}$ (kcal/mol)	24.1	28.5	30.0	43.5	60.8
$\Delta E_{LUMO-HOMO}$ (a. u.)	6.07	5.33	5.31	4.56	3.61

Increasing Stability

Charge Distribution

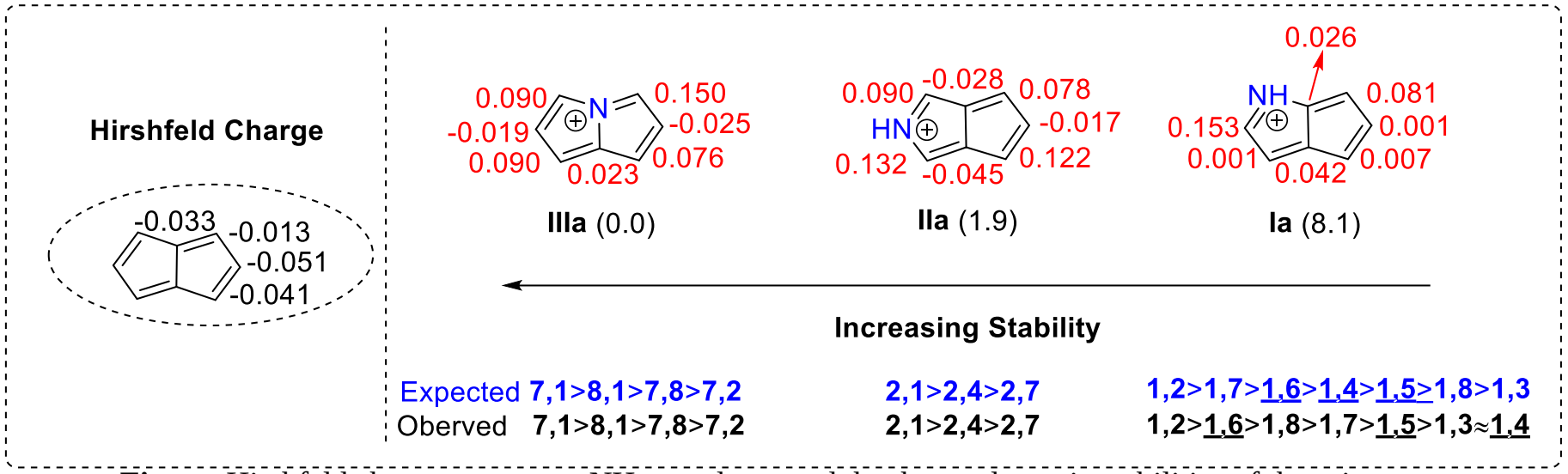


Figure. Hirshfeld charges on parent NH-pentalenes and the thermodynamic stabilities of these isomers.

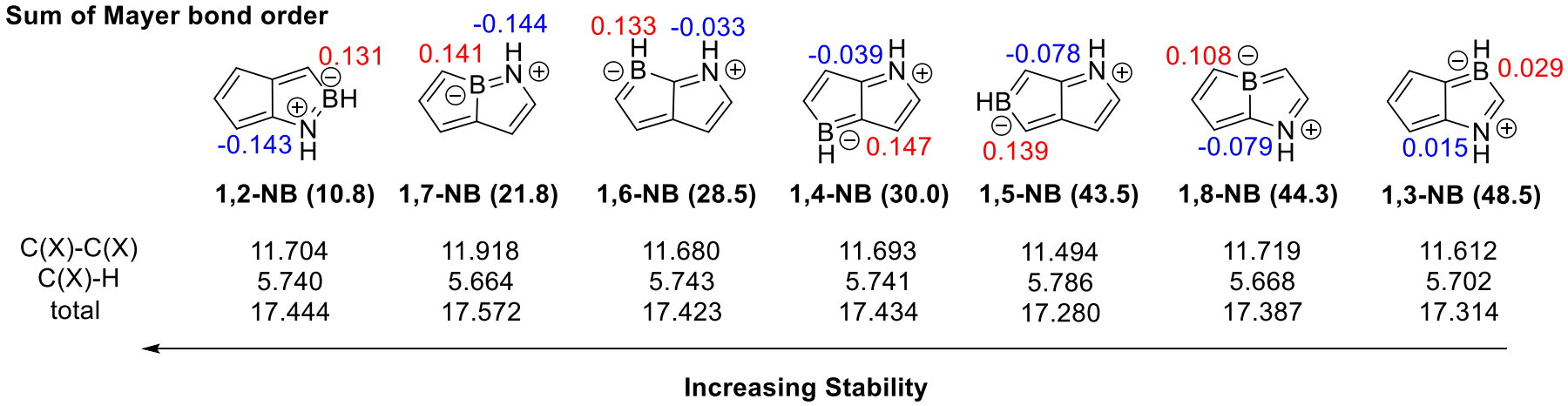
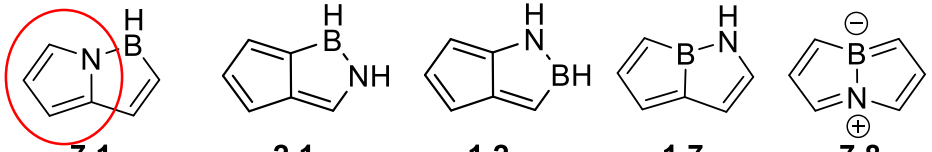


Figure. The sum of Mayer bond orders.

K. AlKaabi, P. L. Dasari and R. Hoffmann, *J Am Chem Soc*, 2012, **134**, 12252.

Aromatic and Stability

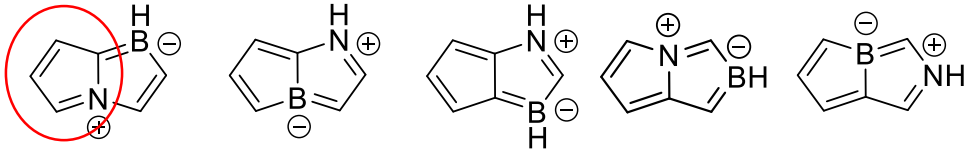
1,2-series



	7,1	**2,1**	**1,2**	**1,7**	**7,8**
$\Delta E_{CCSD(T)}$ (kcal/mol)	0	9.2	10.8	21.8	39.2
NICS(0)$_{\pi zz}$	-3.0/26.3	18.8/31.7	35.6/25.2	53.7/27.9	86.1/122.2
HOMA	0.144/0.677	0.155/0.275	-0.636/-0.146	-1.089/0.083	0.013/-0.039
MCI	0.058/0.016	0.040/0.019	0.019/0.011	0.007/0.011	0.023/0.017

Increasing Stability

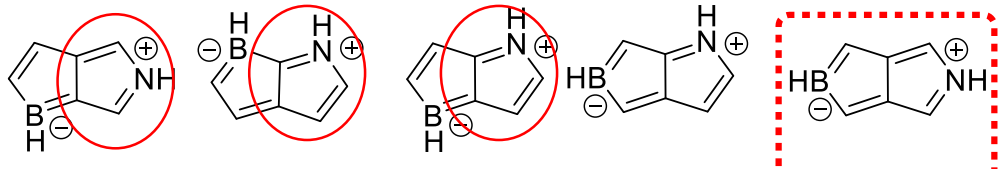
1,3-series



	8,1	**1,8**	**1,3**	**7,2**	**2,7**
$\Delta E_{CCSD(T)}$ (kcal/mol)	20.8	44.3	48.5	52.6	61.7
NICS(0)$_{\pi zz}$	-7.3/28.4	65.7/42.9	48.7/60.4	111.4/133.8	-----
HOMA	0.881/ 0.065	-1.267/ 0.306	0.512/-0.105	0.130/0.206	-0.824/0.264
MCI	0.072/0.014	0.006/0.012	0.060/0.017	0.026/ 0.024	0.009/0.026

Increasing Stability

1,4-series



	2,4	**1,6**	**1,4**	**1,5**	**2,5**
$\Delta E_{CCSD(T)}$ (kcal/mol)	24.1	28.5	30.0	43.5	60.8
NICS(0)$_{\pi zz}$	28.6/-10.1	52.0/-13.8	48.4/-14.1	88.2/46.9	213.8/155.2
HOMA	-0.311/0.756	-0.523/0.961	-0.564/0.8687	-1.043/-0.303	0.156/0.696
MCI	0.012/0.069	0.010/0.081	0.010/ 0.076	0.008/0.011	0.021/0.051

Increasing Stability

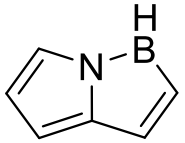
Reactivity

$$\chi = -\frac{E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}}{2} \qquad \varpi = \frac{\chi^2}{2\eta} \qquad N = \frac{1}{\varpi}$$

Isomer	E_{LUMO}	E_{HOMO}	$\Delta E_{LUMO-HOMO}$	χ	ω	N	μ
pentalene	-1.88	-6.78	4.9	4.33	1.91	0.52	
7,1	-1.42	-7.1	5.68	4.26	1.56	0.63	0.305
2,1	-1.58	-7.11	6.53	4.345	1.45	0.69	2.092
1,2	-1.6	-6.93	5.33	4.265	1.71	0.59	0.938
1,7	-1.43	-6.65	5.22	4.04	1.56	0.64	1.360
7,8	-2.21	-6.1	3.89	4.155	2.22	0.45	3.579
8,1	-1.54	-7.32	5.78	4.430	1.70	0.59	1.892
1,6	-1.43	-6.76	5.33	4.095	1.57	0.64	1.986
1,8	-1.6	-6.64	5.04	4.120	1.68	0.59	2.738
1,3	-2.19	-6.63	4.44	4.410	2.19	0.46	5.388
7,2	-2.52	-6.31	3.78	4.415	2.58	0.39	4.432
2,7	-1.73	-6.15	4.42	3.940	1.76	0.57	3.393
2,4	-1.09	-7.16	6.07	4.125	1.40	0.71	3.166
1,4	-1.37	-6.68	5.31	4.025	1.53	0.66	2.856
1,5	-1.72	-6.28	4.56	4.000	1.75	0.57	3.480
2,5	-2.54	-6.14	3.61	4.34	2.61	0.38	5.622

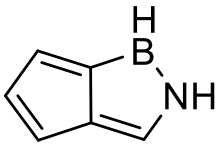
BN-Azulenes

1,2-series



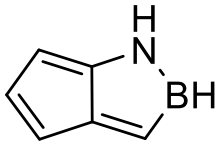
7,1

0



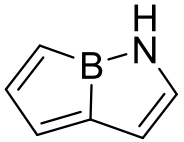
2,1

9.2



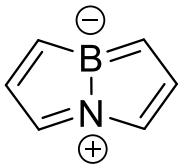
1,2

10.8



1,7

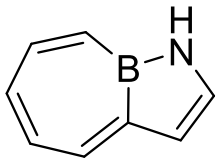
21.8



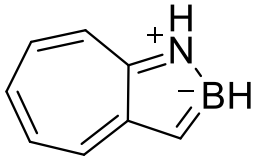
7,8

39.2

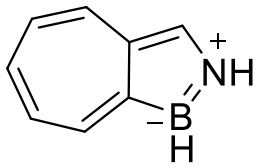
Increasing Stability



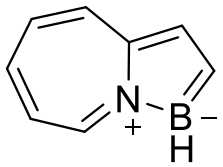
0.0



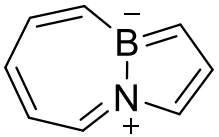
3.3



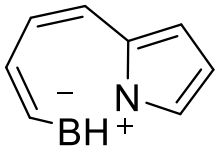
12.8



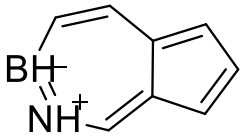
18.7



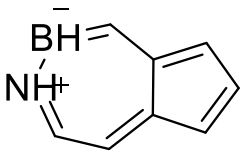
22.0



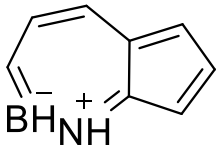
2.1



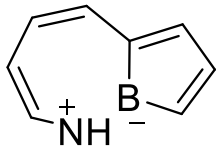
5.8



10.9

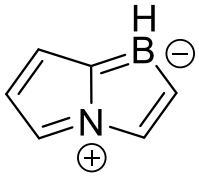


12.9

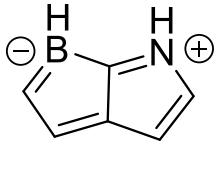


14.2

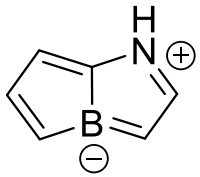
1,3-series



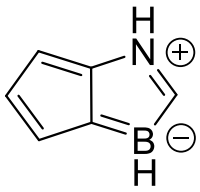
8,1



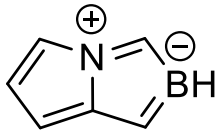
1,6



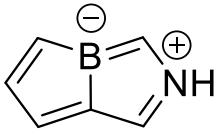
1,8



1,3



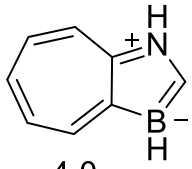
7,2



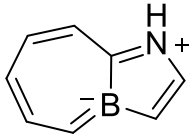
2,7

$\Delta E_{CCSD(T)}$ (kcal/mol)

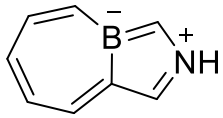
8,1	1,6	1,8	1,3	7,2	2,7
20.8	28.5	44.3	48.5	52.6	61.7



4.0



19.3



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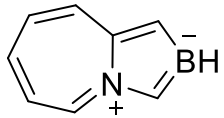
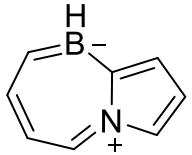
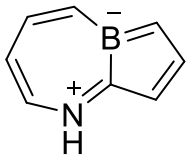


47.7



23.8



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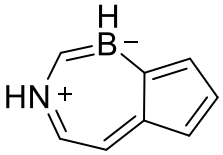
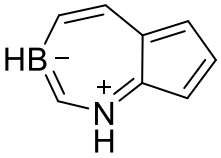


42.5



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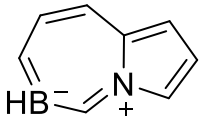

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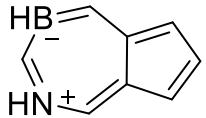

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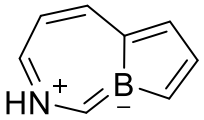

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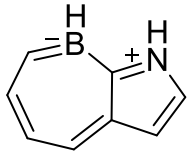
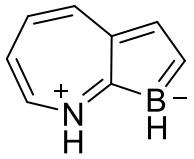
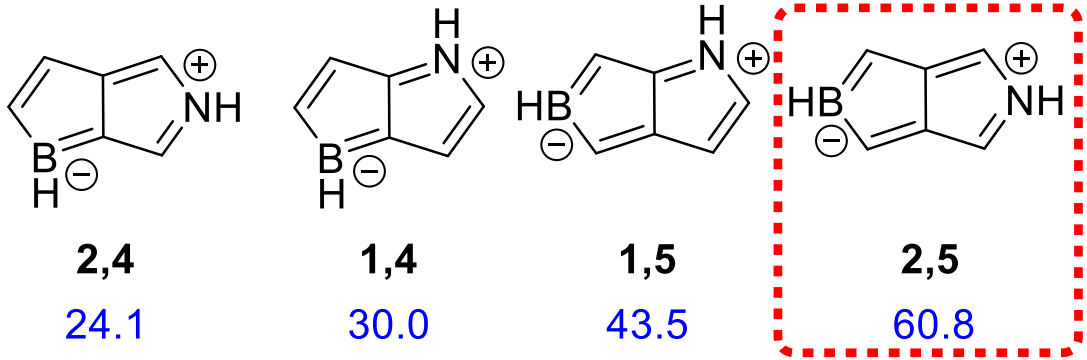


12.1

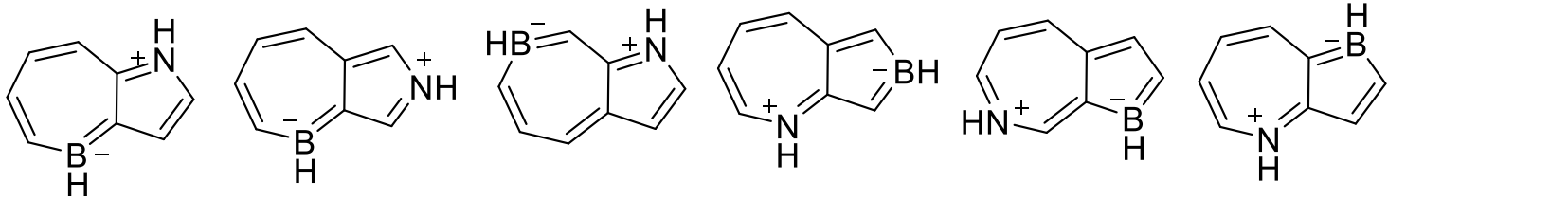


59.0

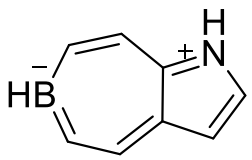
1,4-series



2,4	**1,4**	**1,5**	**2,5**
24.1	30.0	43.5	60.8



1,5-SERIES



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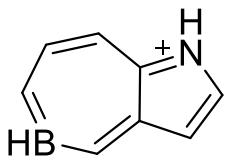
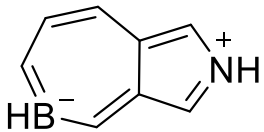


24.8



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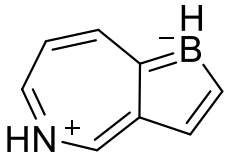

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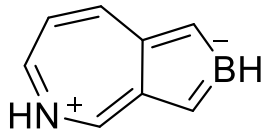
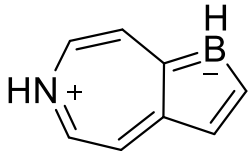
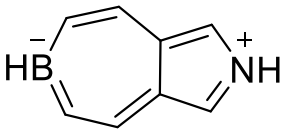


51.3



62.9

1, 6-SERIES



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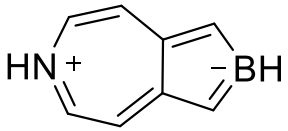
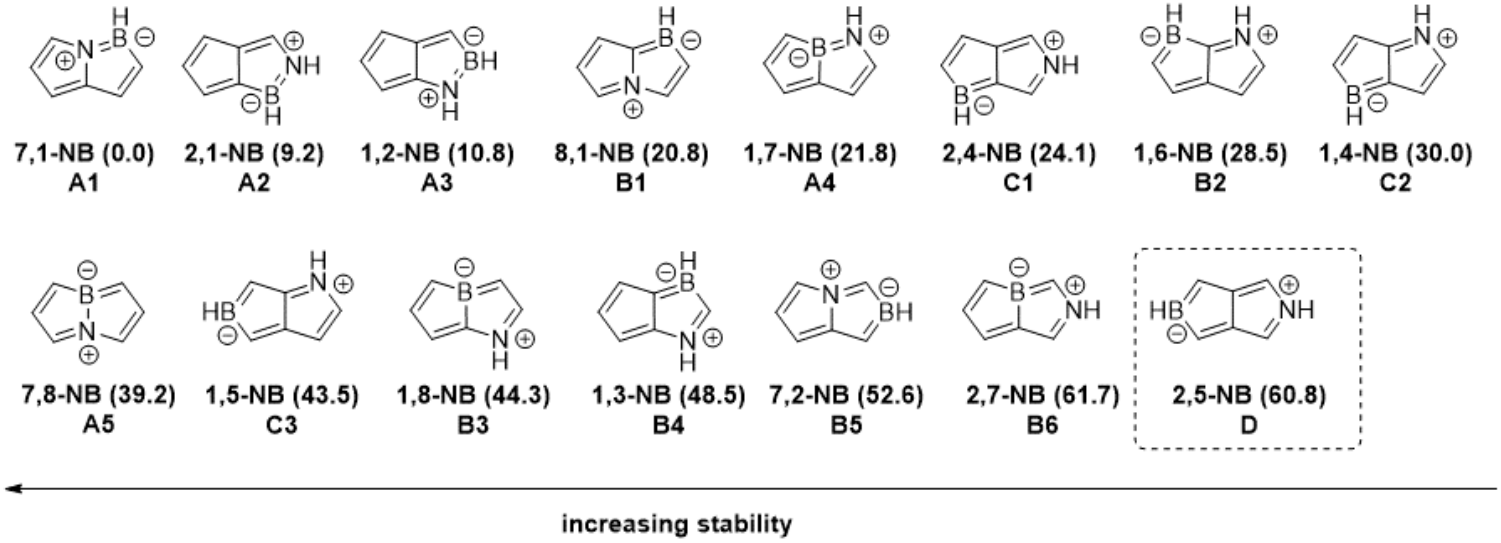


43.9

Current conclusion & Future work

Conclusion



Charge (Hirshfeld) distribution can be used to explain stability of most isomers.
Aromaticity and stability does not have very strong correlation

Future work

- Gobal electrophilicity/nucleophilicity
- Electrostatic potentials
- Dipole moment
- Bond order
- Ring strain
- ……

Recommended Reviews

Recent advances in azaborine chemistry
P. G. Campbell, A. J. Marwitz and S. Y. Liu, *Angew Chem Int Ed*, 2012, **51**, 6074.

B-N versus C-C: how similar are they?
Z. Liu and T. B. Marder, *Angew Chem Int Ed*, 2008, **47**, 242.

A hybrid organic/inorganic benzene
A. J. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon and S. Y. Liu, *Angew Chem Int Ed*, 2009, **48**, 973.

B-N as a C-C substitute in aromatic systems
M. J. D. Bosdet and W. E. Piers, *Can J Chem*, 2009, **87**, 8.

New advances in nanographene chemistry
A. Narita, X. Y. Wang, X. Feng and K. Mullen, *Chem Soc Rev*, 2015, **44**, 6616.

Recent Developments in Azaborinine Chemistry
G. Bélanger-Chabot, H. Braunschweig and D. K. Roy, *Eur. J. Inorg. Chem.*, 2017, **2017**, 4353.

Thanks for your listening

Happy National Day!!!