



*College of Chemistry and Chemical Engineering, Xiamen University*

# Probing Structure-Stability Relationship of Mono BN-doped Phenanthrene Isomers

**Speaker:** Yuanyuan Li

**Advisor:** Jun Zhu

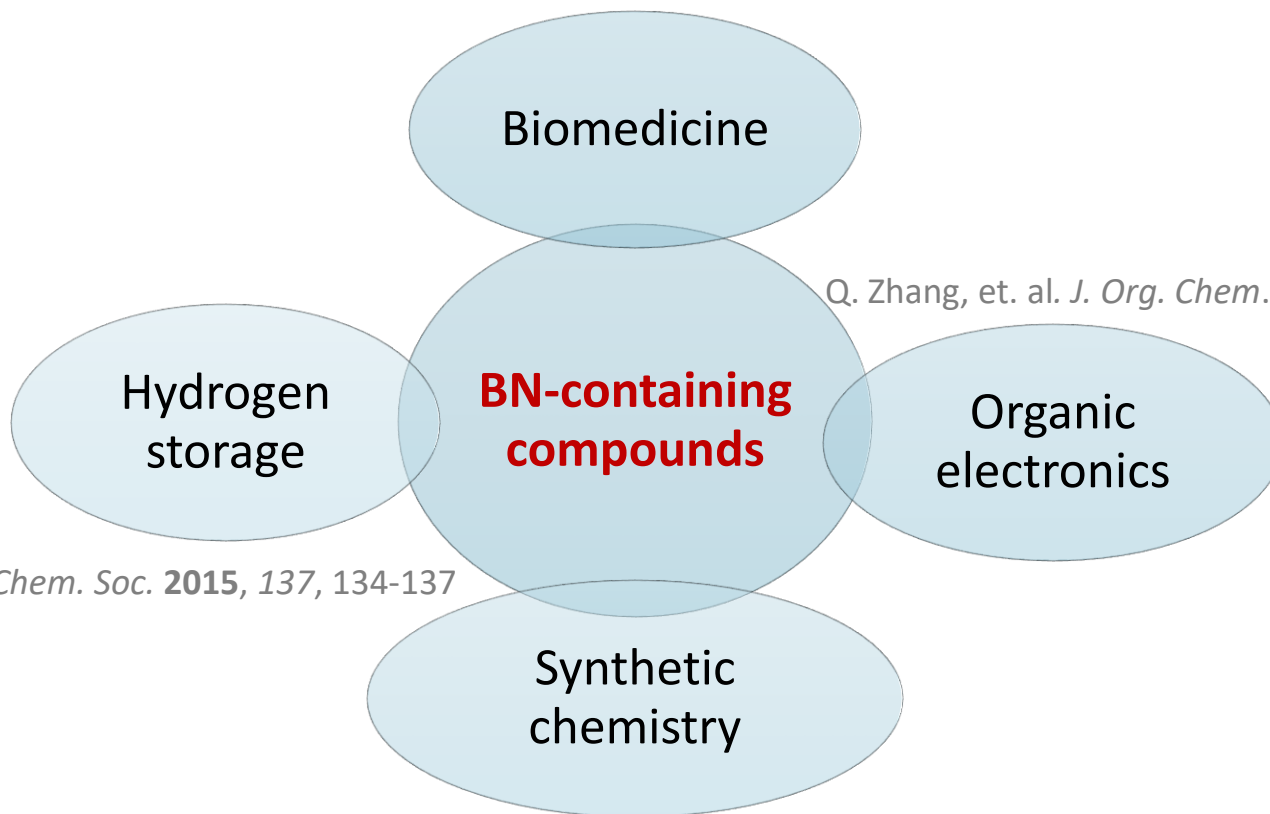
**Date:** 2018.11.20

# Outline

- ◆ Introduction
- ◆ Motivation
- ◆ Computational Details
- ◆ Results and Discussion
- ◆ Conclusions

# 1. Introduction -----The Application of BN-containing compounds

J. Heider, et. al. *Angew. Chem. Int. Ed.* **2013**, 52, 2599-2601.

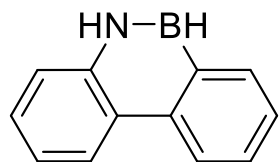


Q. Zhang, et. al. *J. Org. Chem.* **2015**, 80, 196-203

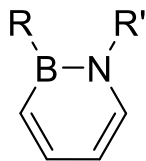
S. Y. Liu, et. al. *J. Am. Chem. Soc.* **2015**, 137, 134-137

S. Y. Liu, J. et. al. *Am. Chem. Soc.* **2016**, 138, 14566-14569

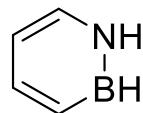
# 1. Introduction -----The history of BN aromatic compounds



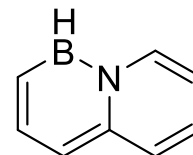
Dewar  
1958



Dewar  
1962

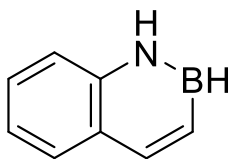


Liu  
2009



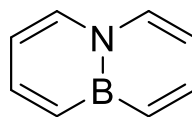
Liu  
2016

1959



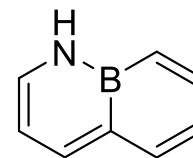
Dewar

1964



Dewar

2015

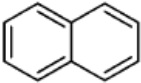
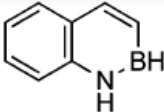
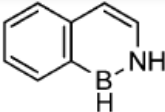
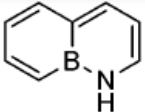
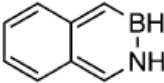
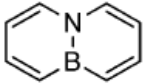
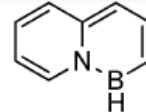


Liu

- M. J. S. Dewar, et. al. *J. Chem. Soc.* **1958**, 3073–3076.  
M. J. S. Dewar, et. al. *J. Chem. Soc.* **1959**, 2728–2730.  
M. J. S. Dewar, et. al. *J. Am. Chem. Soc.* **1962**, 84, 3782.  
M. J. S. Dewar, et. al. *J. Am. Chem. Soc.*, **1964**, 86, 5698-5699.  
S. Y. Liu , et. al. *Angew. Chem. Int. Ed.* **2009**, 121, 991-995.  
S. Y. Liu , et. al. *J. Am. Chem. Soc.* **2015**, 137, 8932–8935  
S. Y. Liu, et. al. *Chem. Eur. J.* 2016, **22**, 12972.

# 1. Introduction-----Theoretical study for BN aromatic compounds

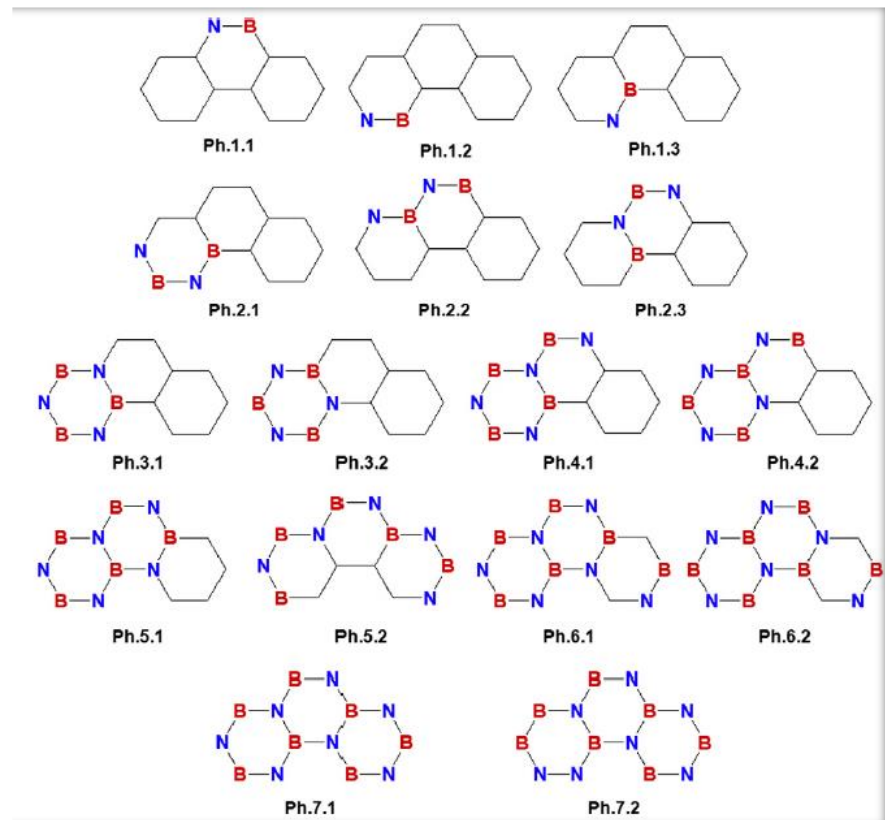
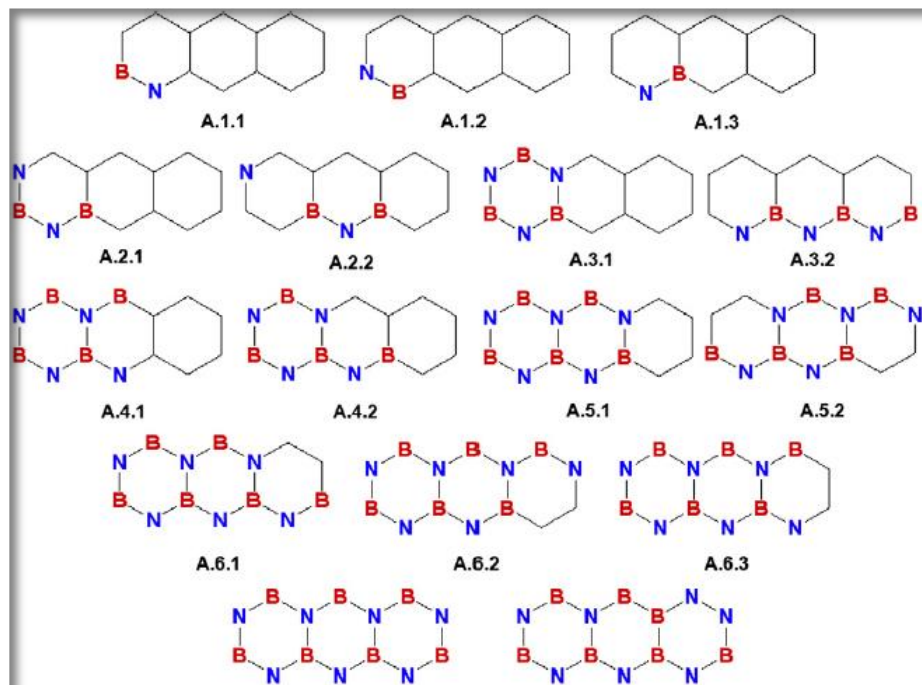
## Mono BN-substituted analogues of naphthalene: a theoretical analysis of the effect of BN position on stability, aromaticity and frontier orbital energies

Compound							
Isomer		1,2	2,1	1,10	2,3	5,10	10,1
$E_{\text{rel}}$		0.00	0.40	7.87	10.68	12.85	17.96
$E_{\text{LUMO}}$	-1.40	-1.51	-1.04	-1.87	-1.83	-1.33	-1.56
$E_{\text{HOMO}}$	-6.15	-6.45	-5.97	-5.89	-5.59	-6.28	-5.55
$\Delta E_{\text{HOMO-LUMO}}$	4.75	4.93	4.93	4.02	3.76	4.94	3.99
$\text{NICS}(0)_{\text{rzz}}$	-33.62/-33.62	-35.75/-19.46	-35.65/-18.67	-22.30/-28.78	-25.75/-28.73	-25.52/-25.51	-24.97/-30.37
HOMA	0.782/0.782	0.906/0.617	0.872/0.561	0.490/0.782	0.517/0.731	0.636/0.636	0.673/0.814
PDI	0.076/0.076	0.082/0.052	0.085/0.053	0.062/0.067	0.064/0.074	0.068/0.068	0.063/0.068

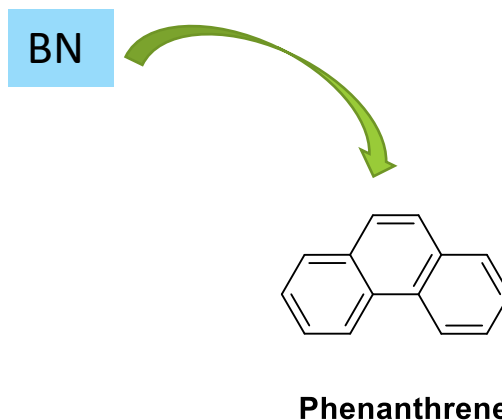
- ✓ The orientational isomers have similar aromaticity, HOMO-LUMO gaps and stability.
- ✓ Placing the BN pair in one ring results in better stability and larger HOMO-LUMO gaps than it in separate rings.
- ✓ The aromaticity of heterocyclic rings is more or less reduced relative to naphthalene.

# 1. Introduction-----Theoretical study for BN aromatic compounds

Boron–nitrogen- and boron-substituted anthracenes and -phenanthrenes as models for doped carbon-based materials



## 2. Motivation



- Which is the most stable isomer?
- Which is the least stable isomer?
- Is there a general rule of stability?
- What factors affect the stability?

# 3. Computational Details

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- Package: Gaussian 09 D.01
- Optimization and frequency: M06-2X/6-311G(d,p)
- Single-point energy: CCSD(T)/6-311G(d,p)



# 4. Results and Discussion

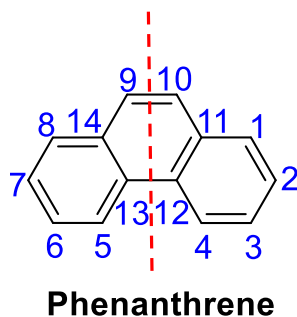
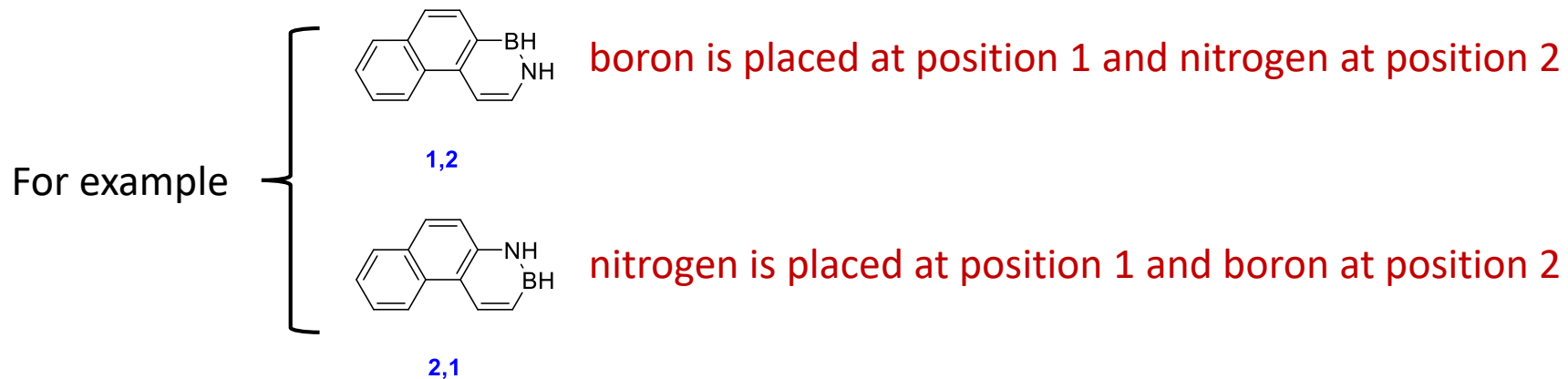
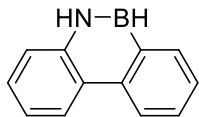


Figure 1 Numbering system for phenanthrene in this study.



# 4. Results and Discussion

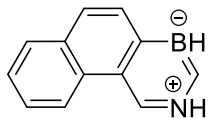
1, 2-series



10,9

No C between B and N

1, 3-series

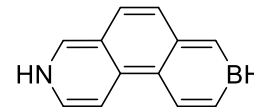


1,3

At least one C between B and N

.....

1, 8-series



2,7

Six C between B and N

Based on the relative positions of B and N, the 91 isomers are classified into seven series:

**1, 2-series** (1,2, 1,11, 2,1, 2,3, 3,2, 3,4, 4,3, 4,12, 10,9, 10,11, 11,1, 11,10, 11,12, 12,4, 12,11 and 12,13)

**1, 3-series** (1,3, 1,10, 1,12, 2,4, 2,11, 3,1, 3,12, 4,2, 4,11, 4,13, 10,1, 10,12, 10,14, 11,2, 11,4, 11,9, 11,13, 12,1, 12,3, 12,5, 12,10 and 12,14 )

**1, 4-series** (1,4, 1,9, 1,13, 2,10, 2,12, 3,11, 3,13, 4,1, 4,5, 4,10, 4,14, 10,2, 10,4, 10,8, 10,13, 11,3, 11,5, 11,14, 12,2, 12,6, 12,8, and 12,9)

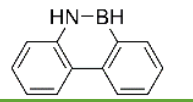
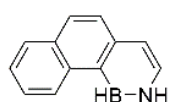
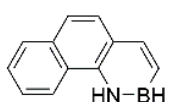
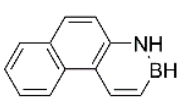
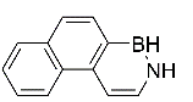
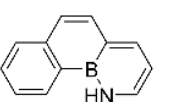
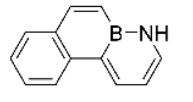
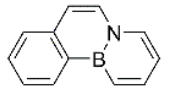
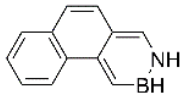
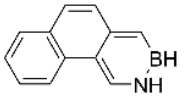
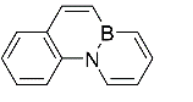
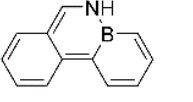
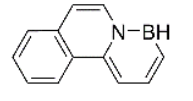
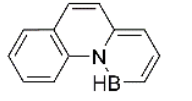
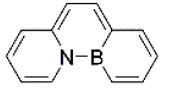
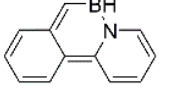
**1, 5-series** (1,5, 1,14, 2,9, 2,13, 3,5, 3,10, 3,14, 4,6, 4,8, 4,9, 10,3, 10,5, 10,7, 11,6, 11,8, and 12,7)

**1, 6-series** (1,6, 1,8, 2,5, 2,14, 3,6, 3,8, 3,9, 4,7, 10,6, and 11,7)

**1, 7-series** (1,7, 2,6, 2,8 and 3,7)

**1, 8-series** (2,7)

# Properties of each series

1,2-series						
Isomer	<b>10,9</b>	<b>4,3</b>	<b>3,4</b>	<b>2,1</b>	<b>1,2</b>	<b>12,4</b>
$\Delta E_a$	0.0	3.7	4.1	4.4	4.4	6.0
$\Delta E_b$	0.0	3.7	4.1	4.4	4.4	6.0
$E_{LUMO}$	-0.34	-0.45	-0.59	-0.65	-0.48	-0.75
$E_{HOMO}$	-7.28	-7.03	-7.07	-7.08	-6.85	-6.73
$\Delta E_{LUMO-HOMO}$	6.93	6.58	6.48	6.43	6.38	5.98
NICS(1)zz	-27.9/-8.5/-29.5	-30.0/-25.1/-16.9	-29.7/-24.8/-17.1	-29.8/-24.4/-17.4	-30.2/-25.4/-16.6	-30.3/-10.9/-23.6
						
	<b>11,1</b>	<b>12,11</b>	<b>3,2</b>	<b>2,3</b>	<b>11,12</b>	<b>11,10</b>
	7.4	10.4	11.2	11.6	14.4	16.6
	7.4	10.4	11.2	11.6	14.4	16.6
	-0.74	-0.31	-0.70	-0.75	-0.50	-1.20
	-6.93	-7.17	-6.70	-6.82	-7.31	-6.46
	6.19	6.86	6.00	6.07	6.81	5.26
	-29.0/-11.0/-23.5	-30.7/-13.4/-20.3	-28.9/-10.7/-23.9	-28.5/-10.7/-24.3	-29.6/-13.6/-19.6	-24.4/-26.9/-25.5
						
	<b>1,11</b>	<b>4,12</b>	<b>12,13</b>	<b>10,11</b>		
	19.2	21.4	23.7	27.8		
	19.2	21.4	23.7	27.8		
	-0.68	-0.82	-1.02	-0.96		
	-6.75	-6.71	-6.48	-6.21		
	6.07	5.89	5.46	5.25		
	-27.9/-8.0/-23.4	-28.0/-7.4/-23.2	-19.1/-25.8/-24.3	-23.8/-26.1/-21.2		

← Increasing stability

The  $\Delta E_a$  (kcal mol<sup>-1</sup>) is the relative energy of each series for comparison.

The  $\Delta E_b$  (kcal mol<sup>-1</sup>) is the energy relative to the most stable isomer.

HOMO/LUMO energies (eV), and NICS(1)zz values (ppm) of BN doped phenanthrene.

# Properties of each series

1,3-series

Isomer

$\Delta E_a$

$\Delta E_b$

$E_{LUMO}$

$E_{HOMO}$

$\Delta E_{LUMO-HOMO}$

NICS(1)zz

<b>12,1</b>	<b>12,3</b>	<b>11,4</b>	<b>11,2</b>	<b>4,2</b>	<b>12,10</b>
0.0	1.3	2.1	3.2	4.6	4.8
32.3	33.6	34.5	35.5	37.0	37.1
-0.96	-0.74	-0.98	-0.73	-0.64	-1.22
-6.52	-6.60	-6.73	-6.68	-6.68	-6.40
5.56	5.85	5.75	5.96	6.04	5.18
-31.2/-16.4/-27.8	-31.3/-16.4/-28.2	-29.2/-16.5/-27.5	-29.6/-16.4/-27.8	-30.1/-20.4/-26.0	-29.4/-25.3/-26.0
<b>3,1</b>	<b>1,3</b>	<b>2,4</b>	<b>11,9</b>	<b>12,5</b>	<b>4,11</b>
5.6	5.6	5.9	6.3	12.3	13.6
37.9	38.0	38.2	38.6	44.6	45.9
-0.89	-0.73	-0.88	-1.09	-1.36	-0.82
-6.71	-6.63	-6.86	-6.67	-6.19	-6.52
5.83	5.90	5.98	5.57	4.82	5.70
-30.2/-18.3/-27.4	-30.2/-20.8/-26.1	-29.3/-18.6/-27.5	-28.9/-24.5/-27.6	-27.7/-25.7/-29.2	-28.2/-12.8/-27.0
<b>12,14</b>	<b>1,10</b>	<b>2,11</b>	<b>10,1</b>	<b>1,12</b>	<b>3,12</b>
14.7	15.1	15.5	15.5	15.8	16.8
47.0	47.4	47.8	47.9	48.1	49.2
-1.04	-1.50	-0.89	-1.39	-1.15	-1.07
-6.38	-6.14	-6.79	-5.93	-6.49	-6.71
5.34	4.64	5.90	4.54	5.35	5.64
-21.8/-26.9/-27.3	-27.4/-16.5/-31.7	-27.9/-12.6/-27.7	-27.9/-24.5/-27.8	-28.1/-13.7/-27.7	-28.2/-13.1/-28.0
<b>10,14</b>	<b>11,13</b>	<b>10,12</b>	<b>4,13</b>		
17.8	18.2	20.4	25.7		
50.2	50.5	52.8	58.0		
-0.82	-1.19	-1.25	-1.36		
-6.45	-6.46	-6.22	-6.08		
5.62	5.26	4.97	4.73		
-20.7/-22.5/-30.6	-21.9/-26.8/-25.8	-25.3/-25.7/-23.9	-21.8/-17.2/-32.5		

← Increasing stability

# Properties of each series

1,4-series

Isomer

$\Delta E_a$

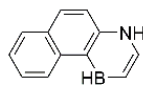
$\Delta E_b$

$E_{LUMO}$

$E_{HOMO}$

$\Delta E_{LUMO-HOMO}$

NICS(1)zz



**4,1**

0.0

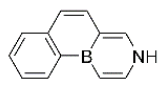
27.2

-0.48

-7.20

6.72

-30.2/-23.6/-17.8



**12,2**

0.3

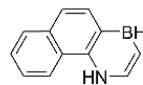
27.6

-0.41

-6.73

6.31

-30.3/-17.2/-22.0



**1,4**

0.8

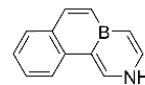
28.0

-0.50

-7.08

6.57

-29.9/-24.3/-17.5



**11,3**

2.4

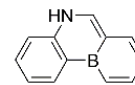
29.6

-0.47

-7.12

6.65

-28.9/-10.7/-21.9



**12,9**

3.5

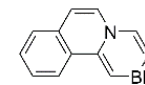
30.7

-0.80

-6.82

6.02

-30.6/-18.6/-18.2



**3,11**

14.4

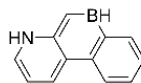
41.6

-0.54

-7.04

6.49

-28.1/-6.7/-21.6



**10,8**

14.5

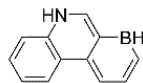
41.7

-1.04

-6.49

5.46

-15.3/-13.1/-30.7



**1,9**

15.2

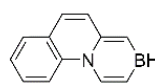
42.4

-1.03

-6.43

5.39

-27.8/-8.2/-22.0



**2,12**

16.3

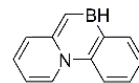
43.6

-0.89

-7.12

6.23

-26.7/-6.1/-22.6



**10,13**

18.9

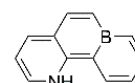
46.2

-0.86

-6.72

5.85

-12.4/-17.2/-29.2



**11,5**

19.1

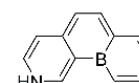
46.3

-1.32

-6.40

5.08

-22.3/-20.9/-21.1



**12,6**

19.3

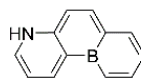
46.5

-1.10

-6.15

5.04

-20.8/-26.7/-25.2



**12,8**

20.0

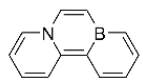
47.3

-1.32

-6.16

4.84

-23.8/-24.8/-25.9



**11,14**

20.6

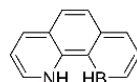
47.9

-0.93

-6.54

5.60

-16.4/-24.7/-22.0



**4,5**

21.6

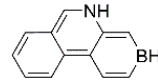
48.8

-1.54

-5.98

4.44

-18.6/-13.4/-26.6



**2,10**

24.0

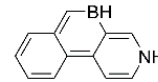
51.3

-1.63

-6.30

4.67

-19.7/-19.1/-28.3



**10,2**

24.6

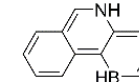
51.8

-1.20

-5.81

4.61

-21.3/-27.0/-22.5



**4,10**

24.6

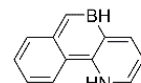
51.8

-1.58

-6.04

4.47

-21.3/-17.2/-31.1



**10,4**

25.3

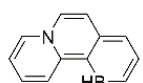
52.5

-1.45

-5.88

4.43

-21.4/-25.2/-25.8



**4,14**

30.8

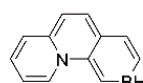
58.1

-1.09

-6.09

5.00

-14.6/-13.6/-28.3



**3,13**

32.4

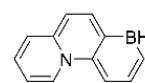
59.6

-1.31

-6.34

5.03

-17.6/-19.8/-25.4



**1,13**

34.1

61.3

-1.33

-6.16

4.83

-20.2/-18.2/-25.8

← Increasing stability

# Properties of each series

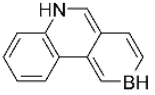
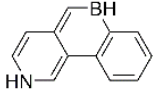
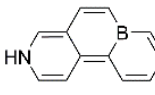
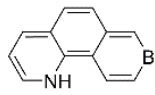
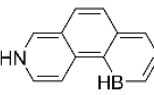
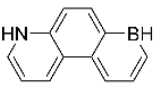
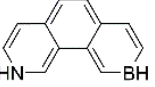
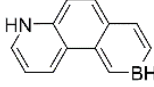
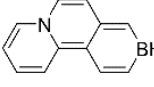
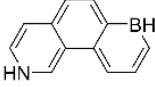
1,5-series

Isomer	<b>12,7</b>	<b>10,5</b>	<b>4,9</b>	<b>11,8</b>	<b>3,10</b>	<b>10,7</b>
$\Delta E_a$	0.0	0.2	0.7	1.2	2.1	2.5
$\Delta E_b$	51.6	51.8	52.3	52.8	53.7	54.1
$E_{LUMO}$	-1.19	-1.38	-1.47	-1.49	-1.53	-1.21
$E_{HOMO}$	-6.00	-6.03	-6.01	-6.07	-6.20	-5.94
$\Delta E_{LUMO-HOMO}$	4.81	4.65	4.54	4.58	4.67	4.73
NICS(1)zz	-25.4/-28.3/-28.9	-20.8/-21.8/-31.1	-27.3/-16.1/-32.4	-26.6/-25.6/-26.9	-27.4/-17.3/-28.6	-20.8/-23.4/-31.5
Isomer	<b>11,6</b>	<b>2,9</b>	<b>10,3</b>	<b>3,5</b>	<b>4,8</b>	<b>4,6</b>
$\Delta E_a$	2.8	3.2	3.9	8.2	8.8	9.0
$\Delta E_b$	54.4	54.9	55.6	59.8	60.4	60.6
$E_{LUMO}$	-1.32	-1.55	-1.22	-1.86	-1.70	-1.52
$E_{HOMO}$	-6.03	-6.17	-5.81	-5.94	-5.62	-5.61
$\Delta E_{LUMO-HOMO}$	4.72	4.62	4.59	4.08	3.92	4.09
NICS(1)zz	-25.4/-27.9/-26.9	-26.7/-17.8/-32.5	-27.7/-26.6/-25.4	-25.6/-20.0/-29.7	-20.3/-15.1/-32.6	-20.4/-17.3/-34.7
Isomer	<b>1,5</b>	<b>1,14</b>	<b>3,14</b>	<b>2,13</b>		
$\Delta E_a$	9.6	13.3	13.7	14.9		
$\Delta E_b$	61.2	64.9	65.3	66.5		
$E_{LUMO}$	-1.89	-1.40	-1.40	-4.19		
$E_{HOMO}$	-5.75	-5.90	-6.05	-6.22		
$\Delta E_{LUMO-HOMO}$	3.86	4.50	4.65	4.73		
NICS(1)zz	-24.5/-17.8/-30.4	-20.8/-17.6/-33.1	-20.8/-19.2/-30.9	-18.9/-19.3/-32.0		

← Increasing stability

# Properties of each series

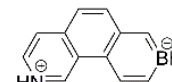
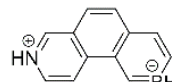
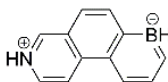
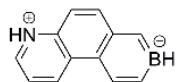
1,6-series

Isomer	<b>3,9</b>	<b>10,6</b>	<b>11,7</b>	<b>2,5</b>	<b>4,7</b>	<b>1,8</b>
$\Delta E_a$	0.0	0.6	5.5	12.8	12.8	16.9
$\Delta E_b$	44.6	45.2	50.1	57.4	57.4	61.5
$E_{LUMO}$	-1.00	-0.62	-1.03	-1.62	-1.24	-1.71
$E_{HOMO}$	-6.76	-6.45	-6.25	-6.21	-5.81	-5.77
$\Delta E_{LUMO-HOMO}$	5.76	5.83	5.22	4.59	4.58	4.06
NICS(1)zz	-28.0/-9.2/-19.4	-12.2/-14.2/-30.8	-19.0/-22.3/-19.6	-15.3/-12.7/-22.9	-13.9/-11.9/-24.7	-18.4/-10.7/-27.6
						
						
	<b>3,6</b>	<b>3,8</b>	<b>2,14</b>	<b>1,6</b>		
	17.0	17.2	17.5	18.3		
	61.7	61.9	62.1	62.9		
	-1.46	-1.68	-1.20	-1.49		
	-5.94	-5.94	-6.36	-5.75		
	4.48	4.26	5.16	4.26		
	-17.0/-15.0/-26.0	-19.0/-12.8/-25.8	-12.0/-15.0/-25.6	-16.7/-12.6/-28.1		

← Increasing stability

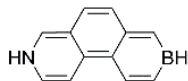
# Properties of each series

## 1,7-series



Isomer	<b>2,8</b>	<b>1,7</b>	<b>3,7</b>	<b>2,6</b>
$\Delta E_a$	0.0	1.1	1.2	1.3
$\Delta E_b$	65.5	66.6	66.7	66.8
$E_{LUMO}$	-1.85	-1.66	-1.64	-1.69
$E_{HOMO}$	-5.81	-5.52	-5.67	-5.78
$\Delta E_{LUMO-HOMO}$	3.95	3.85	4.03	4.09
NICS(1)zz	-19.6/-16.5/-30.9	-22.2/-17.5/-33.6	-23.4/-20.0/-32.6	-19.5/-18.5/-32.6

## 1,8-series



Isomer	<b>2,7</b>
$\Delta E_a$	0.0
$\Delta E_b$	60.3
$E_{LUMO}$	-1.27
$E_{HOMO}$	-6.11
$\Delta E_{LUMO-HOMO}$	4.85
NICS(1)zz	-11.8/-12.6/-21.6

← Increasing stability



# The most/least stable isomers of each series

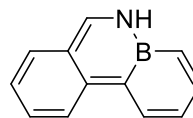
	1,2-series	1,4-series	1,3-series	1,6-series	1,5-series	1,8-series	1,7-series
The most stable compound							
Isomer	<b>10,9</b>	<b>4,1</b>	<b>12,1</b>	<b>3,9</b>	<b>12,7</b>	<b>2,7</b>	<b>2,8</b>
$\Delta E_b$	0.0	27.2	32.3	44.6	51.6	60.3	66.5
$E_{LUMO}$	-0.34	-0.48	-0.96	-1.00	-1.19	-1.27	-1.85
$E_{HOMO}$	-7.28	-7.20	-6.52	-6.76	-6.00	-6.11	-5.81
$\Delta E_{LUMO-HOMO}$	6.93	6.72	5.56	5.76	4.81	4.85	3.95
NICS(1)zz	-27.9/-8.5/-29.5	-30.2/-23.6/-17.8	-31.2/-16.2/-27.8	-28.0/-9.2/-19.4	-25.4/-28.3/-28.9	-11.8/-12.6/-21.6	-19.6/-16.5/-30.9

	1,2-series	1,3-series	1,4-series	1,6-series	1,5-series	1,7-series
The least stable compound						
Isomer	<b>10,11</b>	<b>4,13</b>	<b>1,13</b>	<b>1,6</b>	<b>2,13</b>	<b>2,6</b>
$\Delta E_b$	27.8	58.0	61.3	62.9	66.5	66.8
$E_{LUMO}$	-0.96	-1.36	-1.33	-1.49	-1.49	-1.69
$E_{HOMO}$	-6.21	-6.08	-6.16	-5.75	-6.22	-5.78
$\Delta E_{LUMO-HOMO}$	5.25	4.73	4.83	4.26	4.73	4.09
NICS(1)zz	-23.8/-26.1/-21.2	-21.8/-17.2/-32.5	-20.2/-18.2/-25.8	-16.7/-12.6/-28.1	-18.9/-19.3/-32.0	-19.5/-18.5/-32.6

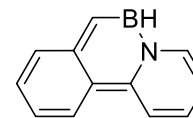
- The stability trend of the most isomers of each series are :  
1, 2-series > 1, 4-series > 1, 3-series > 1, 6-series > 1, 5-series > 1, 8-series > 1, 7-series.
- Separating the BN unit into two rings instead of the BN pair in one ring reduces stability.

# Orientational isomers

**Bridgehead substituted isomers:** one heteroatom at bridgehead position

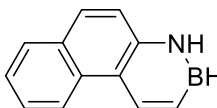


11,10

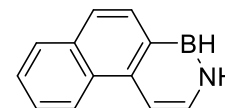


10,11

**Non-bridge substituted isomers:** both B and N atoms at non-bridge positions



2,1



1,2

# Non-bridge substituted isomers

Non-bridge

Isomer	<b>2,1</b>	<b>2,5</b>	<b>3,1</b>	<b>3,7</b>	<b>4,3</b>	<b>3,2</b>	<b>1,10</b>	<b>10,5</b>	<b>2,10</b>	<b>3,9</b>
$\Delta E_b$	4.4	57.4	37.9	66.7	3.7	11.2	47.4	51.8	51.3	44.6
$E_{LUMO}$	-0.65	-1.62	-0.89	-1.64	-0.45	-0.70	-1.50	-1.38	-1.63	-1.00
$E_{HOMO}$	-7.08	-6.21	-6.71	-5.67	-7.03	-6.70	-6.14	-6.03	-6.30	-6.76
$\Delta E_{LUMO-HOMO}$	6.43	4.59	5.83	4.03	6.58	6.00	4.64	4.65	4.67	5.76
NICS(1)zz	-29.8/-24.4/-17.4	-15.3/-12.7/-22.9	-30.2/-18.3/-27.4	-23.4/-20.0/-32.6	-30.0/-25.1/-16.9	-28.9/-10.7/-23.9	-27.4/-16.5/-31.7	-20.8/-21.8/-31.1	-19.7/-19.1/-28.3	-28.0/-9.2/-19.4
	<b>1,2</b>	<b>4,7</b>	<b>1,3</b>	<b>2,6</b>	<b>3,4</b>	<b>2,3</b>	<b>10,1</b>	<b>4,9</b>	<b>10,2</b>	<b>10,6</b>
$\Delta E_b$	4.4	57.4	38.0	66.8	4.1	11.6	47.9	52.3	51.8	45.2
$E_{LUMO}$	-0.48	-1.24	-0.73	-1.69	-0.59	-0.75	-1.39	-1.47	-1.20	-0.62
$E_{HOMO}$	-6.85	-5.81	-6.63	-5.78	-7.07	-6.82	-5.93	-6.01	-5.81	-6.45
$\Delta E_{LUMO-HOMO}$	6.38	4.58	5.90	4.09	6.48	6.07	4.54	4.54	4.61	5.83
NICS(1)zz	-30.2/-25.4/-16.6	-13.9/-11.9/-24.7	-30.2/-20.8/-26.1	-19.5/-18.5/-32.6	-29.7/-24.8/-17.1	-28.5/-10.7/-24.3	-27.9/-24.5/-27.8	-27.3/-16.1/-32.4	-21.3/-27.0/-22.5	-12.2/-14.2/-30.8
	<b>4,10</b>	<b>10,8</b>	<b>10,7</b>	<b>4,8</b>	<b>3,5</b>	<b>4,1</b>	<b>3,8</b>	<b>2,8</b>	<b>4,2</b>	<b>3,10</b>
$\Delta E_b$	51.8	41.7	54.1	60.4	59.8	27.2	61.9	65.5	37.0	53.7
$E_{LUMO}$	-1.58	-1.04	-1.21	-1.70	-1.86	-0.48	-1.68	-1.85	-0.64	-1.53
$E_{HOMO}$	-6.04	-6.49	-5.94	-5.62	-5.94	-7.20	-5.94	-5.81	-6.68	-6.20
$\Delta E_{LUMO-HOMO}$	4.47	5.46	4.73	3.92	4.08	6.72	4.26	3.95	6.04	4.67
NICS(1)zz	-21.3/-17.2/-31.1	-15.3/-13.1/-30.7	-20.8/-23.4/-31.5	-20.3/-15.1/-32.6	-25.6/-20.0/-29.7	-30.2/-23.6/-17.8	-19.0/-12.8/-25.8	-19.6/-16.5/-30.9	-30.1/-20.4/-26.0	-27.4/-17.3/-28.6
	<b>10,4</b>	<b>1,9</b>	<b>2,9</b>	<b>1,5</b>	<b>4,6</b>	<b>1,4</b>	<b>1,6</b>	<b>1,7</b>	<b>2,4</b>	<b>10,3</b>
$\Delta E_b$	52.5	42.4	54.9	61.2	60.6	28.0	62.9	66.6	38.2	55.6
$E_{LUMO}$	-1.45	-1.03	-1.55	-1.89	-1.52	-0.50	-1.49	-1.66	-0.88	-1.22
$E_{HOMO}$	-5.88	-6.43	-6.17	-5.75	-5.61	-7.08	-5.75	-5.52	-6.86	-5.81
$\Delta E_{LUMO-HOMO}$	4.43	5.39	4.62	3.86	4.09	6.57	4.26	3.85	5.98	4.59
NICS(1)zz	-21.4/-25.2/-25.8	-27.8/-8.2/-22.0	-26.7/-17.8/-32.5	-24.5/-17.8/-30.4	-20.4/-17.3/-34.7	-29.9/-24.3/-17.5	-16.7/-12.6/-28.1	-22.2/-17.5/-33.6	-29.3/-18.6/-27.5	-27.7/-26.6/-25.4

The energy differences between the two corresponding non-bridge substituted isomers are very small (0.0-1.8 kcal mol<sup>-1</sup>).

# Bridgehead substituted isomers

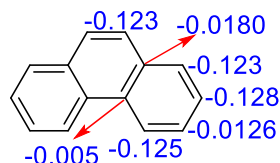
Bridgehead

Isomer	<b>11,6</b>	<b>11,10</b>	<b>11,4</b>	<b>11,9</b>	<b>11,5</b>	<b>11,1</b>	<b>11,7</b>	<b>11,3</b>	<b>11,8</b>	<b>11,2</b>
$\Delta E_b$	54.4	16.6	34.5	38.6	46.3	7.4	50.1	29.6	52.8	35.5
$E_{LUMO}$	-1.32	-1.20	-0.98	-1.09	-1.32	-0.74	-1.03	-0.47	-1.49	-0.73
$E_{HOMO}$	-6.03	-6.46	-6.73	-6.67	-6.40	-6.93	-6.25	-7.12	-6.07	-6.68
$\Delta E_{LUMO-HOMO}$	4.72	5.26	5.75	5.57	5.08	6.19	5.22	6.65	4.58	5.96
NICS(1)zz	-25.4/-27.9/-26.9	-24.4/-26.9/-25.5	-29.2/-16.5/-27.5	-28.9/-24.5/-27.6	-22.3/-20.9/-21.1	-29.0/-11.0/-23.5	-19.0/-22.3/-19.6	-28.9/-10.7/-21.9	-26.6/-25.6/-26.9	-29.6/-16.4/-27.8
	<b>3,14</b>	<b>10,11</b>	<b>4,11</b>	<b>10,14</b>	<b>4,14</b>	<b>1,11</b>	<b>2,14</b>	<b>3,11</b>	<b>1,14</b>	<b>2,11</b>
	65.3	27.8	45.9	50.2	58.1	19.2	62.1	41.6	64.9	47.8
	-1.40	-0.96	-0.82	-0.82	-1.09	-0.68	-1.20	-0.54	-1.40	-0.89
	-6.05	-6.21	-6.52	-6.45	-6.09	-6.75	-6.36	-7.04	-5.90	-6.79
	4.65	5.25	5.70	5.62	5.00	6.07	5.16	6.49	4.50	5.90
	-20.8/-19.2/-30.9	-23.8/-26.1/-21.2	-28.2/-12.8/-27.0	-20.7/-22.5/-30.6	-14.6/-13.6/-28.3	-27.9/-8.0/-23.4	-12.0/-15.0/-25.6	-28.9/-6.7/-21.6	-20.8/-17.6/-33.1	-27.9/-12.6/-27.7
	<b>12,6</b>	<b>12,5</b>	<b>12,8</b>	<b>12,7</b>	<b>12,4</b>	<b>12,9</b>	<b>12,3</b>	<b>12,10</b>	<b>12,1</b>	<b>12,2</b>
	46.5	44.6	47.3	51.6	6.0	30.7	33.6	37.1	32.3	27.6
	-1.10	-1.36	-1.32	-1.19	-0.75	-0.80	-0.74	-1.22	-0.96	-0.41
	-6.15	-6.19	-6.16	-6.00	-6.73	-6.82	-6.60	-6.40	-6.52	-6.73
	5.04	4.82	4.84	4.81	5.98	6.02	5.85	5.18	5.56	6.31
	-20.8/-26.7/-25.2	-27.7/-25.7/-29.2	-23.8/-24.8/-25.9	-25.4/-28.3/-28.9	-30.3/-10.9/-23.6	-30.6/-18.6/-18.2	-31.3/-16.4/-28.2	-29.4/-25.3/-26.0	-31.2/-16.2/-27.8	-30.3/-17.2/-22.0
	<b>3,13</b>	<b>4,13</b>	<b>1,13</b>	<b>2,13</b>	<b>4,12</b>	<b>10,13</b>	<b>3,12</b>	<b>10,12</b>	<b>1,12</b>	<b>2,12</b>
	59.6	58.0	61.3	66.5	21.4	46.2	49.2	52.8	48.1	43.6
	-1.31	-1.36	-1.33	-4.19	-0.82	-0.86	-1.07	-1.25	-1.15	-0.89
	-6.34	-6.08	-6.16	-6.22	-6.71	-6.72	-6.71	-6.22	-6.49	-7.12
	5.03	4.73	4.83	4.73	5.89	5.85	5.64	4.97	5.35	6.23
	-17.6/-19.8/-25.4	-21.8/-17.2/-32.5	-20.2/-18.2/-25.8	-18.9/-19.3/-32.0	-28.0/-7.4/-23.2	-12.4/-17.2/-29.2	-28.2/-13.1/-28.0	-25.3/-25.7/-23.9	-28.1/-13.7/-27.7	-26.7/-6.1/-22.6

The energy differences between the two corresponding bridgehead substituted isomers are much large (10.9-16.0 kcal mol<sup>-1</sup>).

A feature of the more stable isomer always contains B atom at bridgehead position.

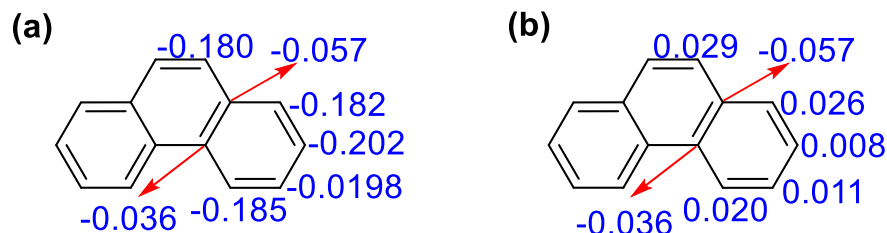
# The ADCH charges



The atomic dipole moment corrected Hirshfeld population (ADCH) charge of phenanthrene.

- ✓ Negative charges are similar on the non-bridge carbon atom and much more than the bridgehead carbon atom.
- ✓ The difference in stability between the non-bridge substituted isomers is small.
- ✓ The bridgehead substituted isomers have a large energy difference due to one heteroatom at the bridgehead position.
- ✓ Placing a highly electronegative nitrogen atom at the non-bridge part and a weakly electronegative boron atom at the bridgehead part would be more stable.

# NBO charges

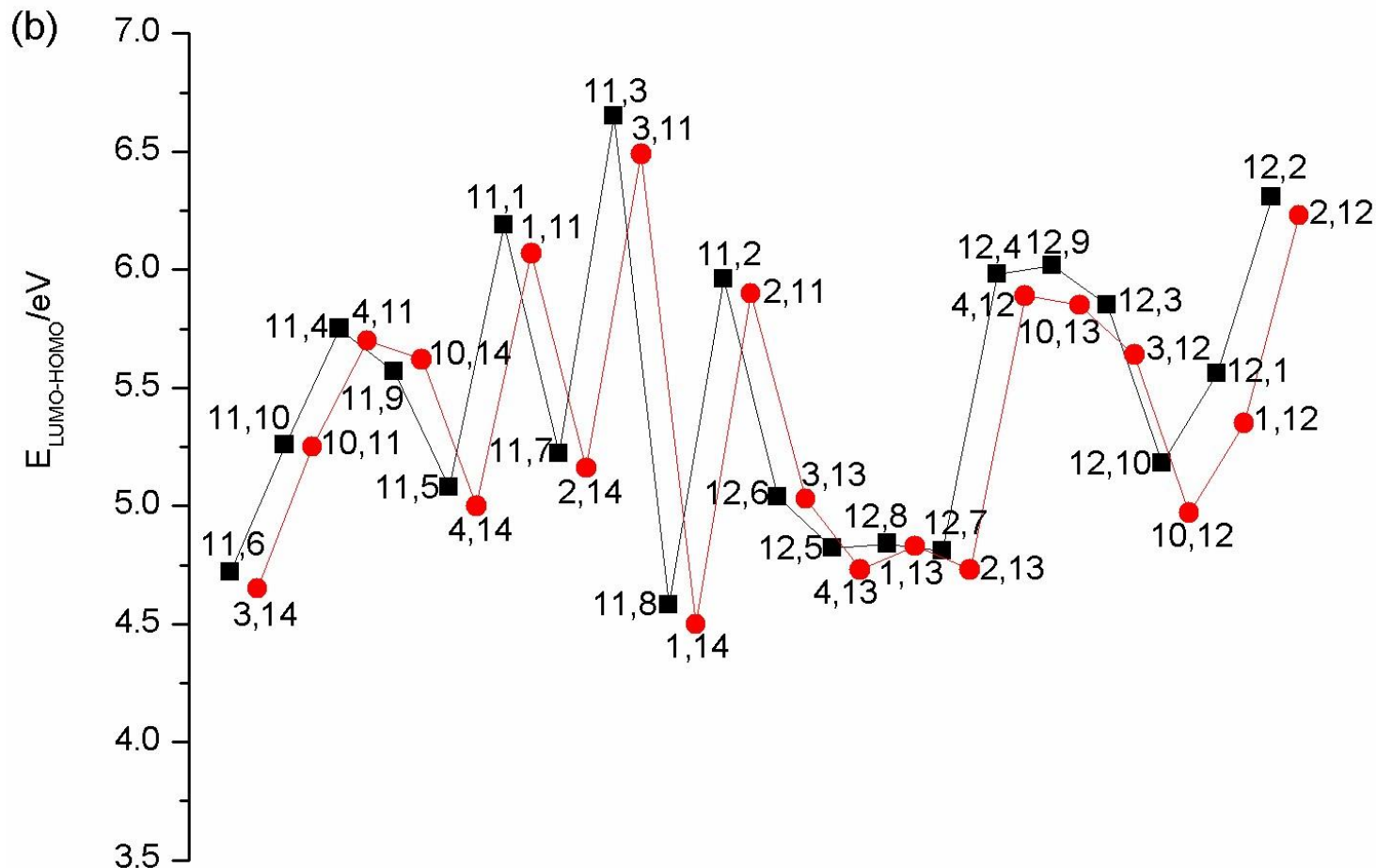


NBO charges of phenanthrene. (a) without adding H atomic charges. (b) H atomic added.

- ✓ Without adding H atomic charges, the NBO charges are consistent with ADCH charges.
- ✓ H atomic added, the NBO charges of non-bridged carbon atoms are positive and the bridgehead carbon atoms are negative.
- ✓ The carbon atoms at the 1, 4 and 10 positions have similar NBO charges and are larger than the carbon atoms at positions 2 and 3.

# HOMO-LUMO energy gap of Bridgehead substituted isomers

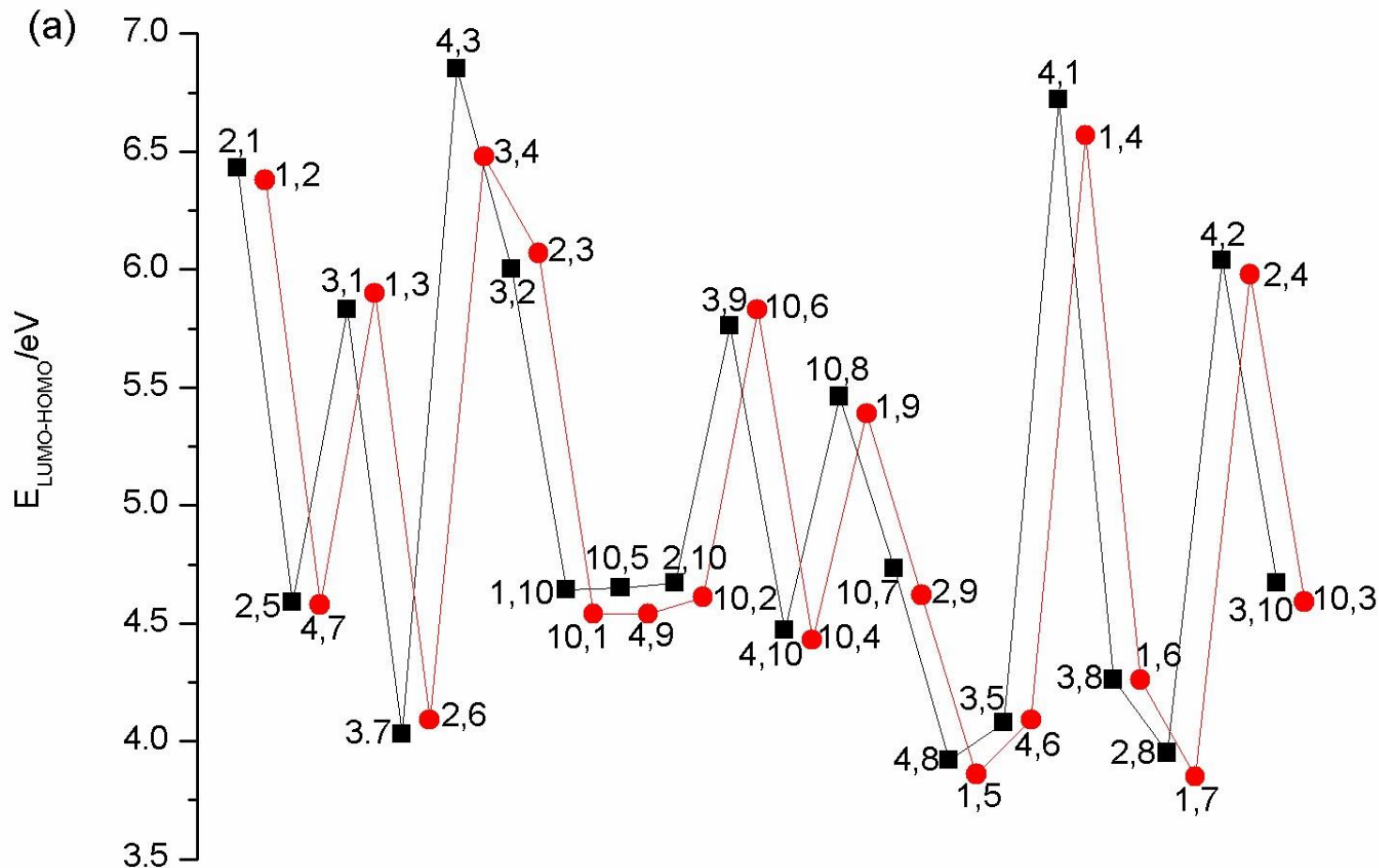
Black/Red line represents lower/higher energy isomers of the two orientational isomers.



The one with lower energy has a larger HOMO-LUMO energy gap (except for **11,9/10,14**).

# HOMO-LUMO energy gap of Non-bridge substituted isomers

Black/Red line represents lower/higher energy isomers of the two orientational isomers.



Except for several pairs of isomers (3,1/1,3, 3,7/2,6, 3,2/2,3, 3,9/10,6 do not follow the rule, and the values of 3,5/4,6 and 3,8/1,6 are almost equal), most non-bridge substituted isomers also follow this rule.



# 5. Conclusions

The orientational isomers have similar stability, HOMO–LUMO gaps and aromaticity

## Stability

- BN in one ring > BN in two rings
- The non-bridge isomers have similar stability.
- B at bridgehead position > N at bridgehead position

## HOMO/LUMO

More stable isomers have larger HOMO-LUMO energy gaps

## Aromaticity

The aromaticity of heterocyclic rings is more or less reduced relative to naphthalene

**Thanks for your kind attention!**

# Question

Determine the valence electron count of the following complexes:

