

Computational details

The molecular structures were optimized by the M062X density functional and 6-311G(d,p) basis set with an ultrafine grid. The frequency calculations were performed at the same level to confirm that all the structures were energy minima. Single point energy calculations were performed at the CCSD(T)/6-311G(d,p) level based on optimized structures. The HOMA index and PDI index were computed by using the Multiwfn program.

Results and discussion

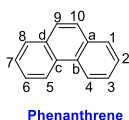


Figure 1 Numbering system for phenanthrene in this study.

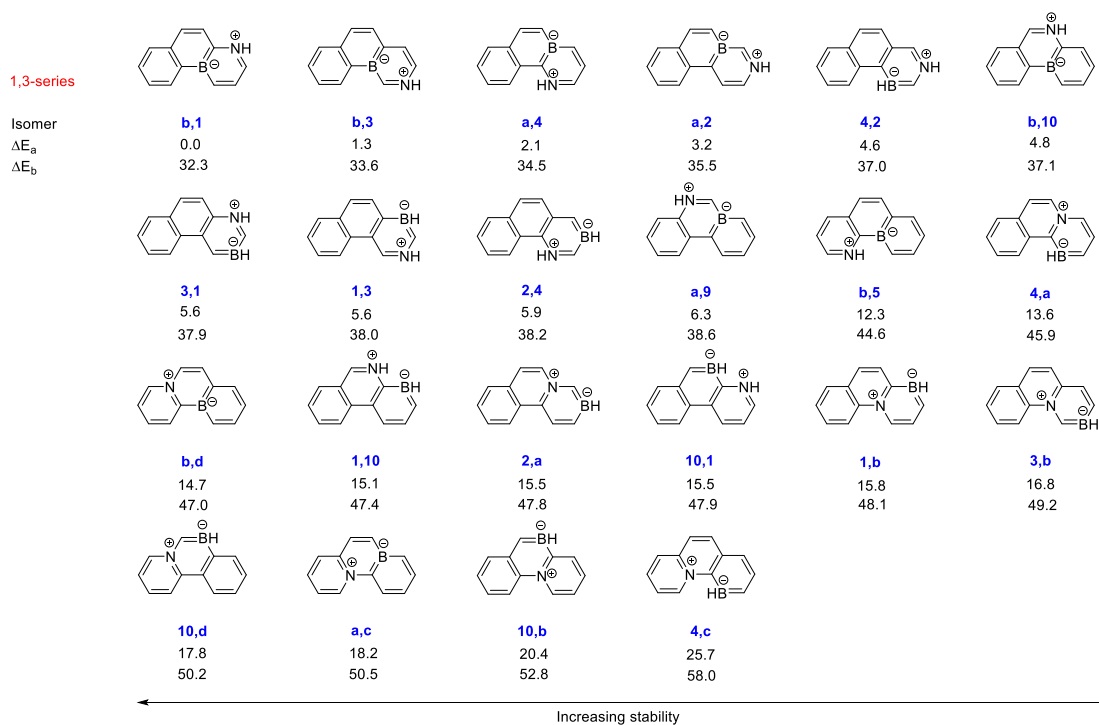
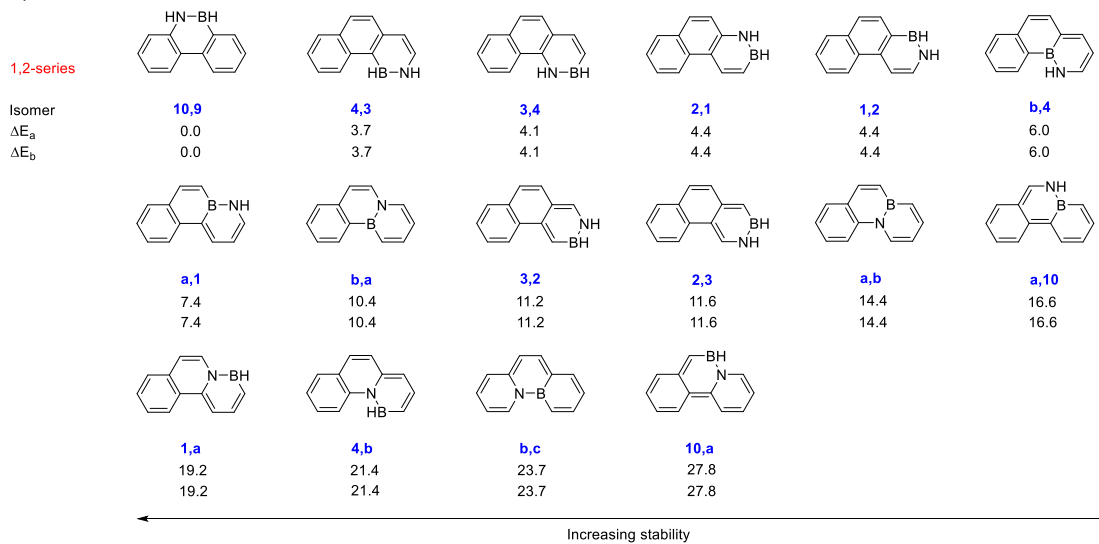
There are 91 isomers of BN doped phenanthrene. In order to avoid repetition, the replacement positions on the phenanthrene have been numbered as shown in Figure 1 (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, a, b, c, d). Based on the relative positions of B and N, the isomers were classified into seven series for comparison, namely 1, 2-series (1,2, 1,a, 2,1, 2,3, 3,2, 3,4, 4,3, 4,b, 10,9, 10,a, a,1, a,10, a,b, b,4, b,a and b,c), 1, 3-series (1,3, 1,10, 1,b, 2,4, 2,a, 3,1, 3,b, 4,2, 4,a, 4,c, 10,1, 10,b, 10,d, a,2, a,4, a,9, a,c, b,1, b,3, b,5, b,10 and b,d), 1, 4-series (1,4, 1,9, 1,c, 2,10, 2,b, 3,a, 3,c, 4,1, 4,5, 4,10, 4,d, 10,2, 10,4, 10,8, 10,c, a,3, a,5, a,d, b,2, b,6, b,8, and b,9), 1, 5-series (1,5, 1,d, 2,9, 2,c, 3,5, 3,10, 3,d, 4,6, 4,8, 4,9, 10,3, 10,5, 10,7, a,6, a,8, and b,7), 1, 6-series (1,6, 1,8, 2,5, 2,d, 3,6, 3,8, 3,9, 4,7, 10,6, and a,7), 1, 7-series (1,7, 2,6, 2,8 and 3,7), and 1, 8-series (2,7), respectively.

Stability analysis

The relative energies of BN doped phenanthrene are shown below. The ΔE_a (kcal mol⁻¹) is the relative energy of each series for comparison. The ΔE_b (kcal mol⁻¹) is the energy relative to the most stable isomer. The ΔE_b span a range of 66.8 kcal mol⁻¹. The most stable isomer is **10,9** and the least stable isomer is **2,6**.

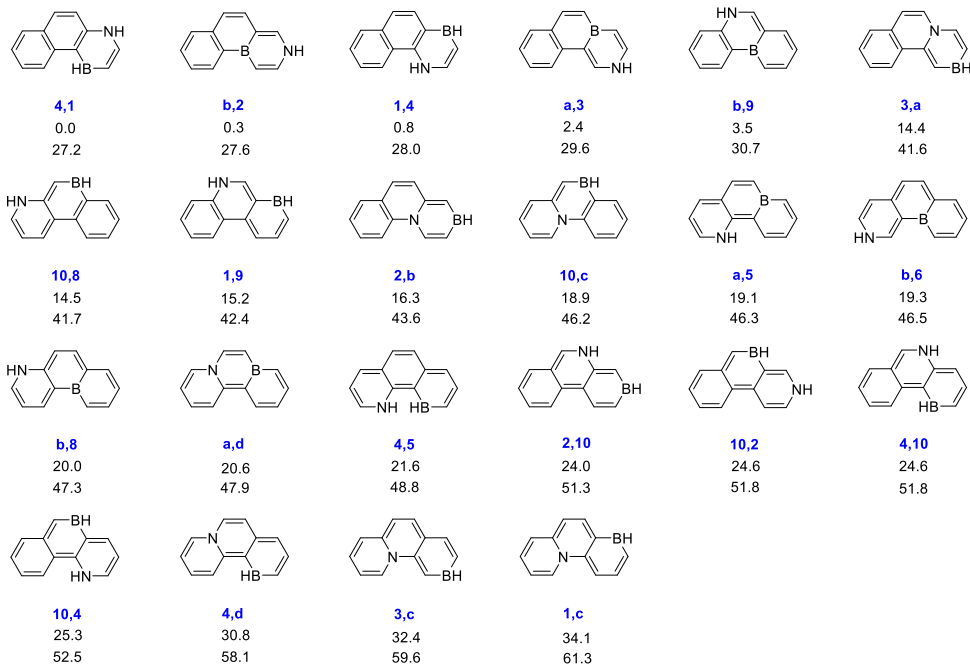
The energies of 1, 2-series isomers are in the range of 0-27.8 kcal mol⁻¹, and the **10,9** isomer in this series is the most stable one of all isomers. The energies of 1, 3-series isomers span a slightly smaller range of 25.7 kcal mol⁻¹, which are higher than the **10,9** isomer of 32.3-58.0 kcal mol⁻¹. The energies of 1,4-series isomers span a range of 34.1 kcal mol⁻¹, which are 27.2-61.3 kcal mol⁻¹ relative to the **10,9** isomer. A narrower range of energies, 14.9 kcal mol⁻¹, is observed for the 1, 5-series isomers, and they are in the range of 51.6-66.5 kcal mol⁻¹ relative to the **10,9** isomer. The energies of 1, 6-series isomers are in the range of 18.3 kcal mol⁻¹, which are 44.6-62.9 kcal mol⁻¹ relative to the **10,9** isomer. The 1,7-series isomers have very small energies differences and range only 1.3 kcal mol⁻¹. However, the energies difference are very large relative to the most stable 10,9 isomers, which are 66.5-66.8 kcal mol⁻¹. The energy of 1, 8-series, **2,7** isomers, is 60.3 kcal mol⁻¹ higher than the most stable **10,9** isomer. The stability

trend of the most isomers of each series : 1, 2-series (**10,9** isomer, 0.0 kcal mol⁻¹) > 1, 4-series (**4,1** isomer, 27.2 kcal mol⁻¹) > 1, 3-series (**b,1** isomer, 32.3 kcal mol⁻¹) > 1, 6-series (**3,9** isomer, 44.6 kcal mol⁻¹) > 1, 5-series (**b,7** isomer, 51.6 kcal mol⁻¹) > 1, 8-series (**2,7** isomer, 60.3 kcal mol⁻¹) > 1, 7-series (**2,8** isomer, 65.5 kcal mol⁻¹). Separating the BN unit into two rings instead of the BN pair in one ring reduces stability. The charge separated 1,3-related **b,1** isomers, the 1,5-related **b,7** isomers and the 1,7-related **2,8**-isomers are less stable than neutral structures.



1,4-series

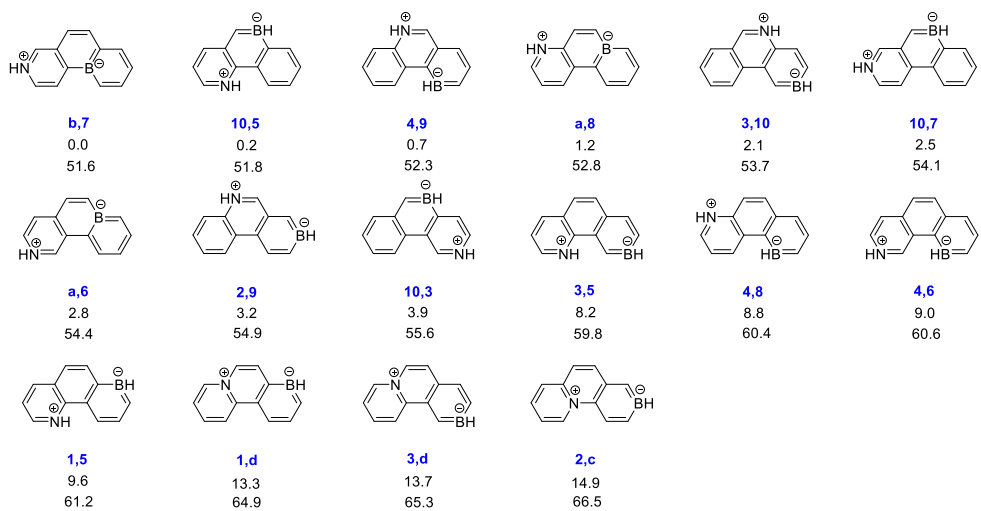
Isomer
 ΔE_a
 ΔE_b



← Increasing stability

1,5-series

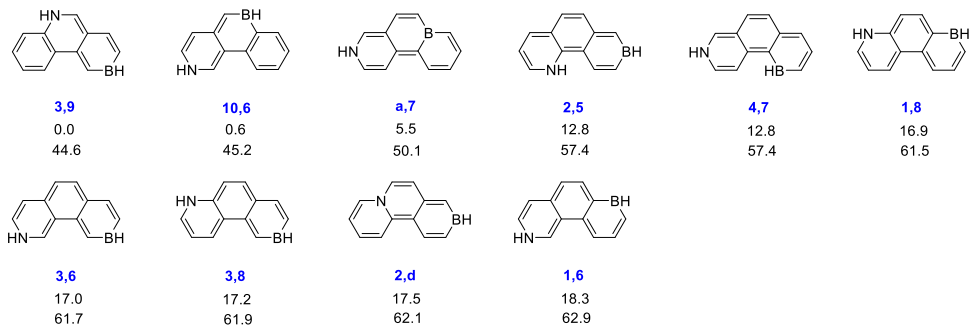
Isomer
 ΔE_a
 ΔE_b



← Increasing stability

1,6-series

Isomer
 ΔE_a
 ΔE_b



← Increasing stability

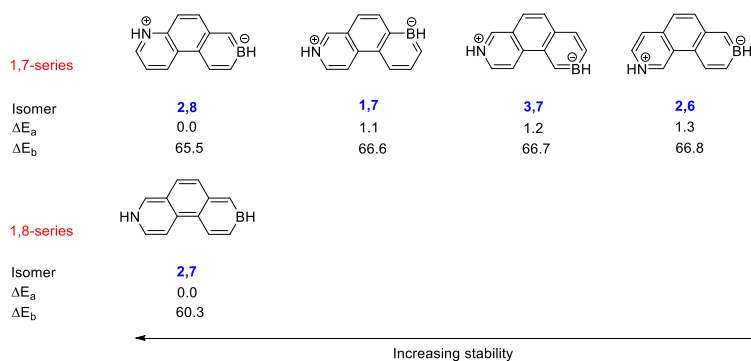


Figure 2 The relative energies of BN doped phenanthrene. The ΔE_a (kcal mol^{-1}) is the relative energy of each series for comparison. The ΔE_b (kcal mol^{-1}) is the energy relative to the most stable isomer.

There are 42 orientational isomers of BN doped phenanthrene. The 20 orientational isomers have both B and N atoms at the external ring positions (**1,10/10,1**, **2,1/1,2**, **2,5/4,7**, **2,8/1,7**, **2,10/10,2**, **3,1/1,3**, **3,2/2,3**, **3,5/4,6**, **3,7/2,6**, **3,8/1,6**, **3,9/10,6**, **3,10/10,3**, **4,1/1,4**, **4,2/2,4**, **4,3/3,4**, **4,8/1,5**, **4,10/10,4**, **10,5/4,9**, **10,7/2,9**, **10,8/1,9**), which are denoted as the external isomers. The 20 orientational isomers have one heteroatom at ring-junction (internal) position (**a,1/1,a**, **a,2/2,a**, **a,3/3,a**, **a,4/4,a**, **a,5/4,d**, **a,6/3,d**, **a,7/2,d**, **a,8/1,d**, **a,9/10,d**, **a,10/10,a**, **b,1/1,b**, **b,2/2,b**, **b,3/3,b**, **b,4/4,b**, **b,5/4,c**, **b,6/3,c**, **b,7/2,c**, **b,8/1,c**, **b,9/10,c**, **b,10/10,b**), which are denoted as the internal isomers. The other two orientational isomers, **b,a/a,b** and **b,d/a,c**, have B and N atoms both at ring-junction position.

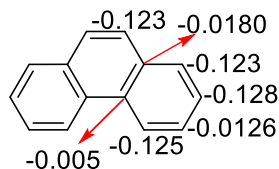


Figure 3 The ADCH charges of phenanthrene.

The energy difference between the two corresponding external isomers is very small ($0.0\text{-}1.8 \text{ kcal mol}^{-1}$). This finding indicates that the external isomers have similar stability. However, the energy difference between the two corresponding internal isomers is much larger ($10.9\text{-}16.0 \text{ kcal mol}^{-1}$). Their stability varies greatly, and a feature of the more stable isomer is that B atom is at ring-junction position rather than N atom of the internal isomers. This phenomenon can be explained by the atomic dipole moment corrected Hirshfeld population (ADCH) charge of phenanthrene. It can be observed that the negative charge on the external carbon atom is more than the internal carbon atom. Placing a highly electronegative nitrogen atom at the external part and a weakly electronegative boron atom at the internal part would be more stable. This also explains that the energy difference between the internal isomers is small and that the boron is more stable at the ring-junction. At the same time, since the charges of the external carbon atoms are similar, the difference in stability between the external isomers is small.