Supplementary Materials

Substitution Effect of a Single Nitrogen Atom on π-Electronic Systems of Linear Polycyclic Aromatic Hydrocarbons (PAHs); Theoretically Visualized Coexistence of Mono- and Poly-cyclic π-Electron Delocalization

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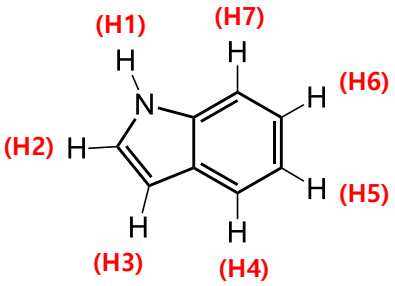
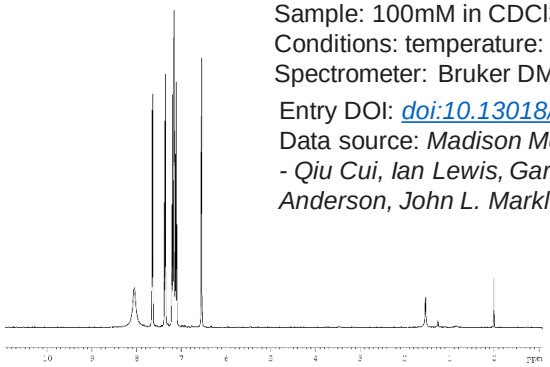
Table S1. Aromaticity indices of the linear tricyclic N-PAHs.

Compound	Location	HOMA	AICD critical isosurface value	NICS(2)
Anthracene	Center C-6MR	0.760	0.081	- 6.69
	Side C-6MR	0.662	0.072	- 5.21
	C-10MR	0.792	0.081	
	C-14MR	0.806	0.082	
Phenanthrene	Center C-6MR	0.511	0.076	- 4.94
	Side C-6MR	0.891	0.077	- 5.44
	C-10MR	0.698	0.076	
	C-14MR	0.779	0.081	
Acridine	Center N-6MR	0.765	0.074	- 6.57
	Side C-6MR	0.664	0.069	- 5.19
	N-10MR (quinoline)	0.797	0.074	
	N-14MR	0.811	0.084	
Phenanthridine	Center N-6MR	0.629	0.075	- 4.89
	C-6MR (C-6MR')	0.902 (0.912)	0.072 (0.079)	- 5.38 (- 5.48)
	N-10MR (N-10MR)'	0.769 (0.762)	0.075 (0.075)	
	N-14MR	0.824	0.075	
Carbazole	Center N-5MR	0.657	0.061	- 4.31
	Side C-6MR	0.958	0.069	- 5.26
	N-9MR (indole)	0.826	0.061	
	N-13MR	0.891	0.078	
Isocarbazole	Center N-5MR	0.725	0.071	- 5.95
	Side C-6MR	0.801	0.072	- 5.25
	Side N-6MR	0.803	0.074	- 4.21
	N-9MR (isoindole)	0.842	0.076	
	N-9MR' (indolizine)	0.839	0.071	
	N-13MR	0.885	0.074	
Pseudocarbazole	Center N-5MR	0.714	0.061	- 5.37
	Side C-6MR	0.917	0.071	- 5.62
	Side N-6MR	0.686	0.073	- 3.31
	N-9MR (indole)	0.845	0.078	
	N-9MR (indolizine)	0.772	0.061	
	N-13MR	0.845	0.073	

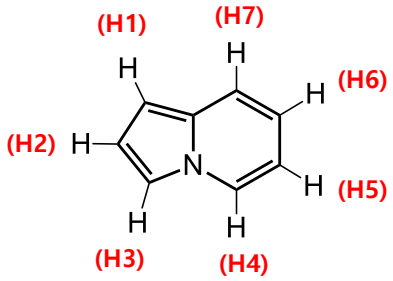


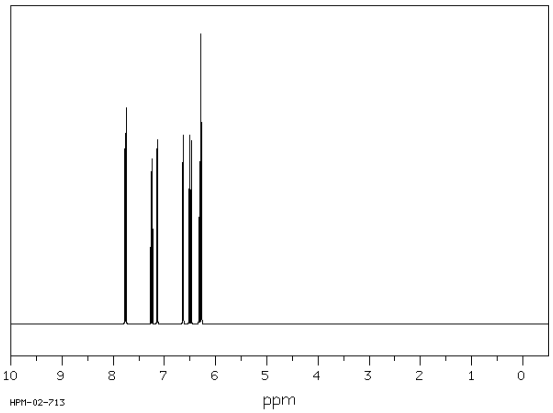


Sample: 100mM in CDCl3, ref: TMS
Conditions: temperature: 298K, pH: n/a
Spectrometer: Bruker DMX - 400MHz

Entry DOI: doi:10.13018/BMSE000097
Data source: *Madison Metabolomics Consortium - Qiu Cui, Ian Lewis, Gareth Westler, Mark E. Anderson, John L. Markley*

	Experiment (NMR)		B3LYP/6-311G(2df, p)	
	Indolizine in $CDCl_3$		Indolizine w/ scrf = CCl_4	
H position	Chemical Shift (ppm)	relative	Chemical Shift (ppm)	relative
H3	6.48	0.00	7.26	0.00
H5	7.05	0.57	7.88	0.62
H2	7.10	0.62	7.90	0.64
H6	7.13	0.64	7.93	0.68
H7	7.30	0.82	8.06	0.80
H4	7.58	1.10	8.35	1.10
H1			8.51	1.25





	Experiment (NMR)		B3LYP/6-311G(2df, p)	
	Indolizine in CCl4		Indolizine w/ scrf = CCl4	
H position	Chemical Shift (ppm)	relative	Chemical Shift (ppm)	relative
H1	6.28	0.00	7.14	0.00
H5	6.31	0.03	7.20	0.05
H6	6.50	0.22	7.34	0.20
H2	6.64	0.36	7.54	0.40
H3	7.14	0.86	7.98	0.83
H7	7.25	0.97	8.03	0.89
H4	7.76	1.48	8.60	1.45

Entry DOI: doi.org/10.1071/CH9641128
Black, P.; Heffernan, M.; Jackman, L.; Porter, Q.; Underwood, G., Proton Magnetic Resonance Spectra of Indolizine and Its Methyl Derivatives and Aza Analogues. *Australian Journal of Chemistry* **1964**, *17*, 1128-1137.

Figure S1. H-NMR comparisons between experimental and theoretical (GIAO-B3LYP/6-311G(2df,p)) results of indole and indolizine.

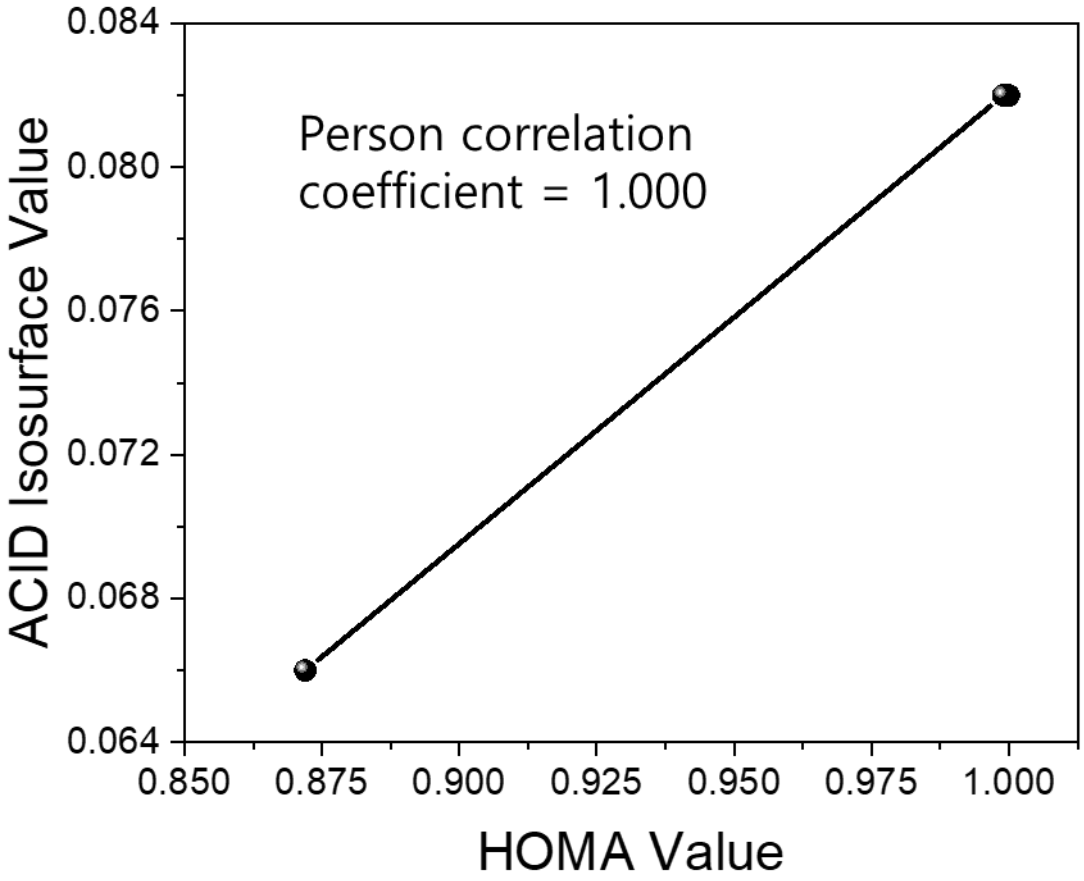
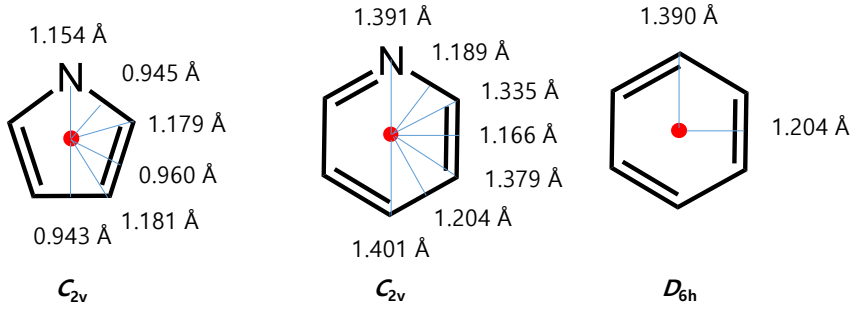


Figure S2. Correlation between HOMA and ACID values of monocycles.



	Averaged Distance (reduced distance compared to those of benzene)		
center – atom	1.175 Å (- 15.5 %)	1.370 Å (- 1.44 %)	1.390 Å
center – bond	0.949 Å (- 21.2 %)	1.186 Å (- 1.47 %)	1.204 Å

Figure S3. Averaged distance from atoms and covalent bonds to the center (NICS probe).

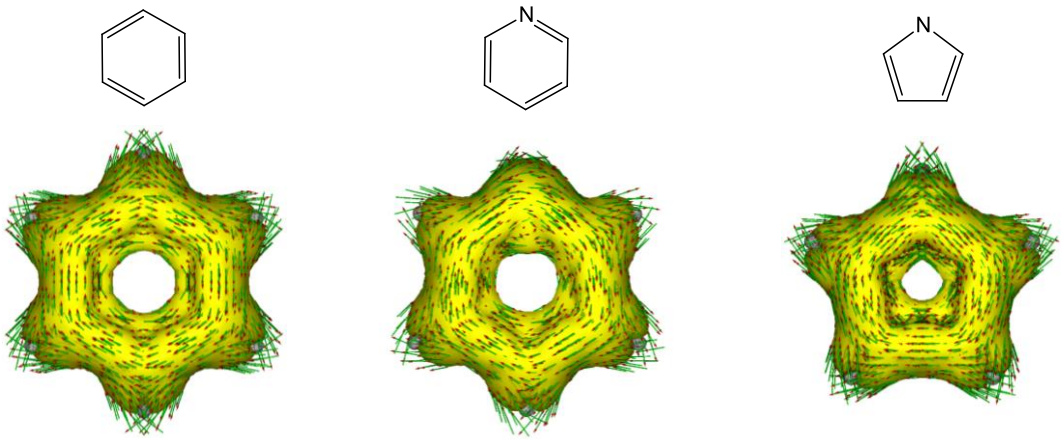


Figure S4. Magnetic induced current maps of six- and five-membered monocycles; benzene, pyridine, and pyrrole.

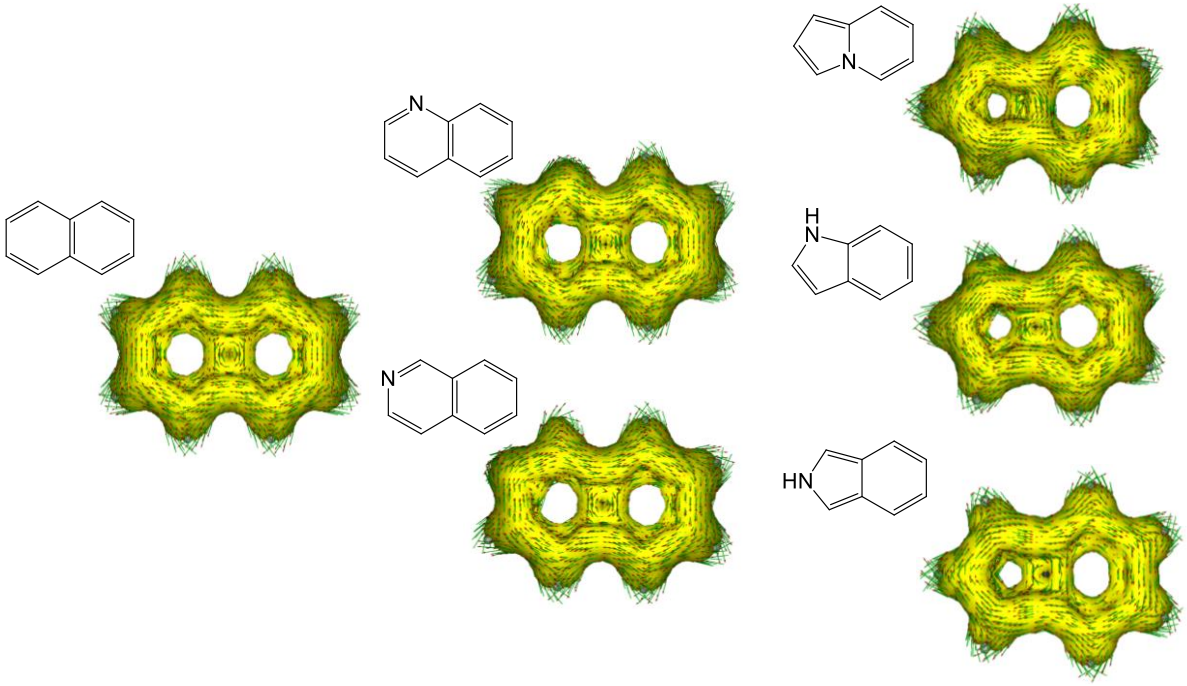


Figure S5. Magnetic induced current maps of fused bicycles with constituent six- and five-membered rings.

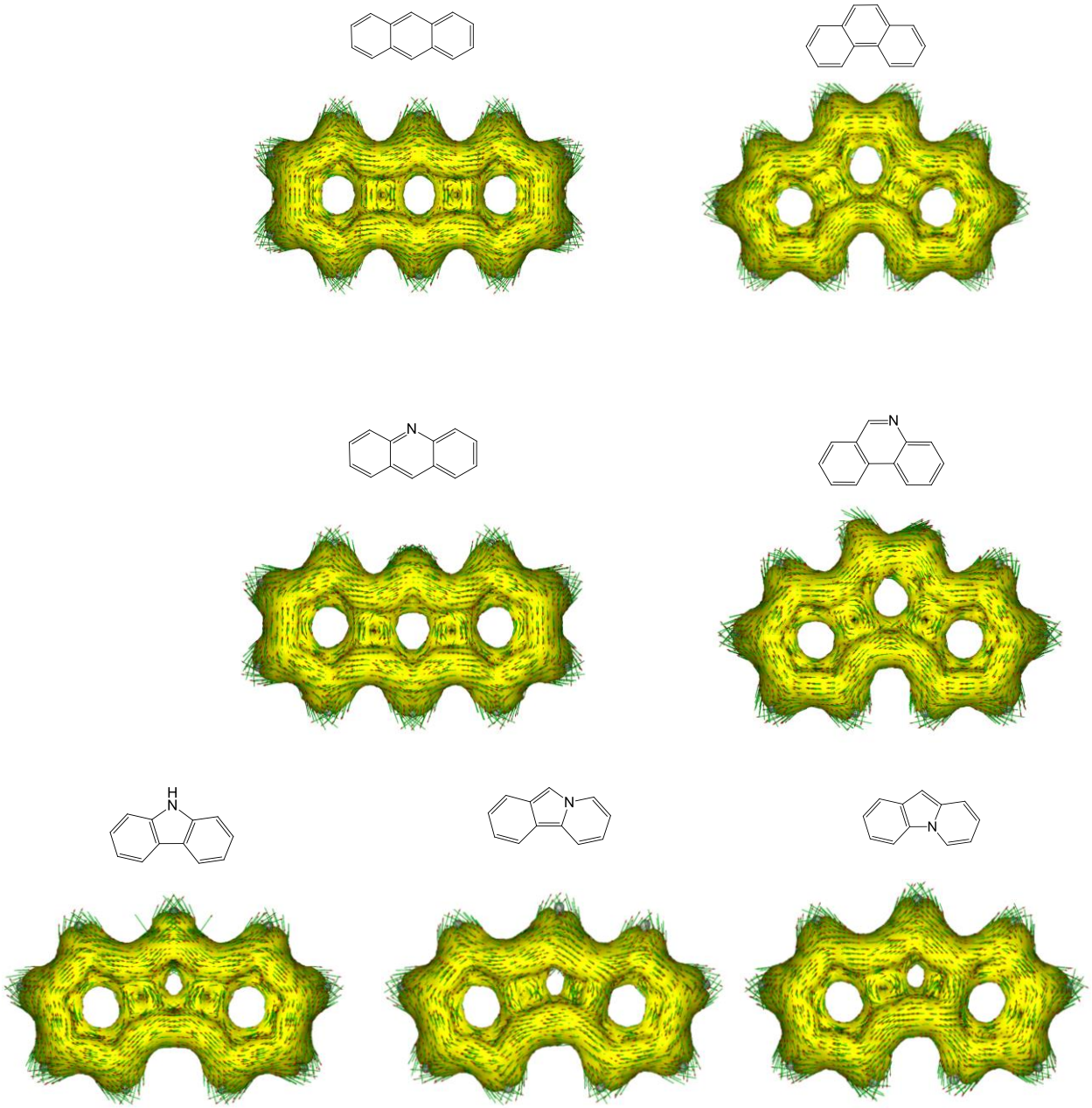
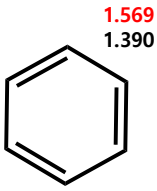
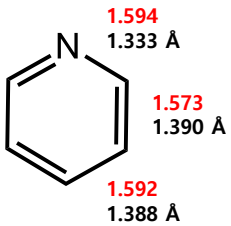


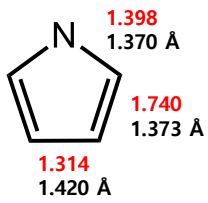
Figure S6. Magnetic induced current maps of fused tricycles with constituent six- and five-membered rings.



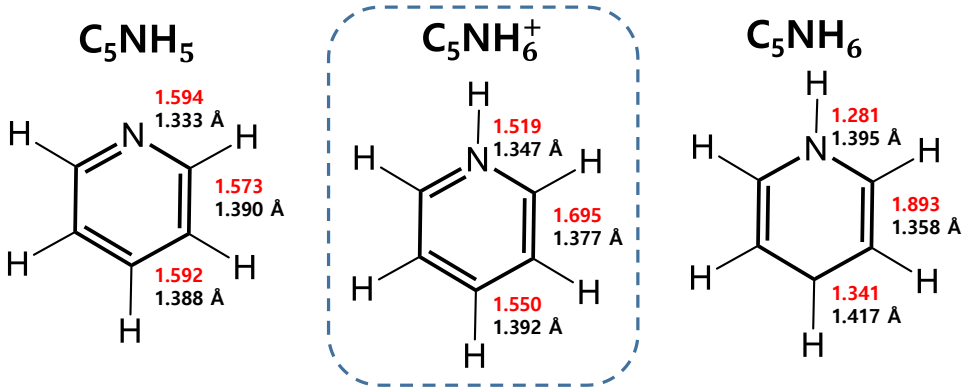
E	0.001
G	0.000
H	0.999



E	0.000
G	0.000
H	1.000



E	0.022
G	0.107
H	0.872

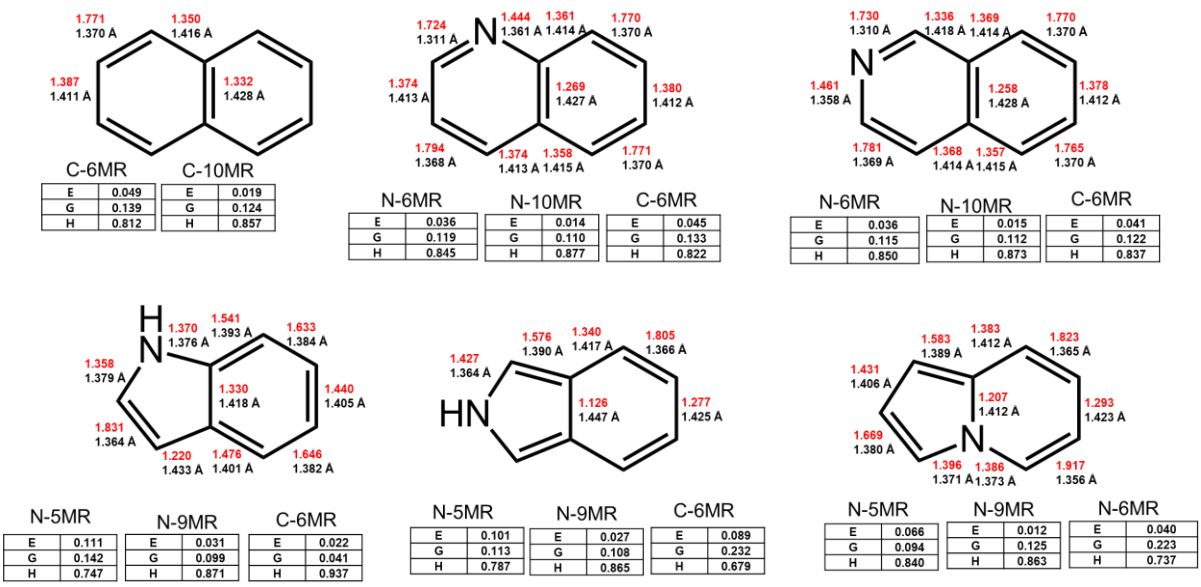


E	0.000
G	0.000
H	1.000

E	0.000
G	0.017
H	0.983

E	0.038
G	0.227
H	0.735

Figure S7. Bond lengths (black), Pauling bond numbers (red), and HOMA parameters of monocycles and N-6MRs with different charge states.



C-6MR	
E	0.049
G	0.139
H	0.812

C-10MR	
E	0.019
G	0.124
H	0.857

N-6MR	
E	0.036
G	0.119
H	0.845

N-10MR	
E	0.014
G	0.110
H	0.877

C-6MR	
E	0.045
G	0.133
H	0.822

N-6MR	
E	0.036
G	0.115
H	0.850

N-10MR	
E	0.015
G	0.112
H	0.873

C-6MR	
E	0.041
G	0.122
H	0.837

N-5MR	
E	0.111
G	0.142
H	0.747

N-9MR	
E	0.031
G	0.099
H	0.871

C-6MR	
E	0.022
G	0.041
H	0.937

N-5MR	
E	0.101
G	0.113
H	0.787

N-9MR	
E	0.027
G	0.108
H	0.865

C-6MR	
E	0.089
G	0.232
H	0.679

N-5MR	
E	0.066
G	0.094
H	0.840

N-9MR	
E	0.012
G	0.125
H	0.863

N-6MR	
E	0.040
G	0.223
H	0.737

Figure S8. Bond lengths (black), Pauling bond numbers (red), and HOMA parameters of bicycles.

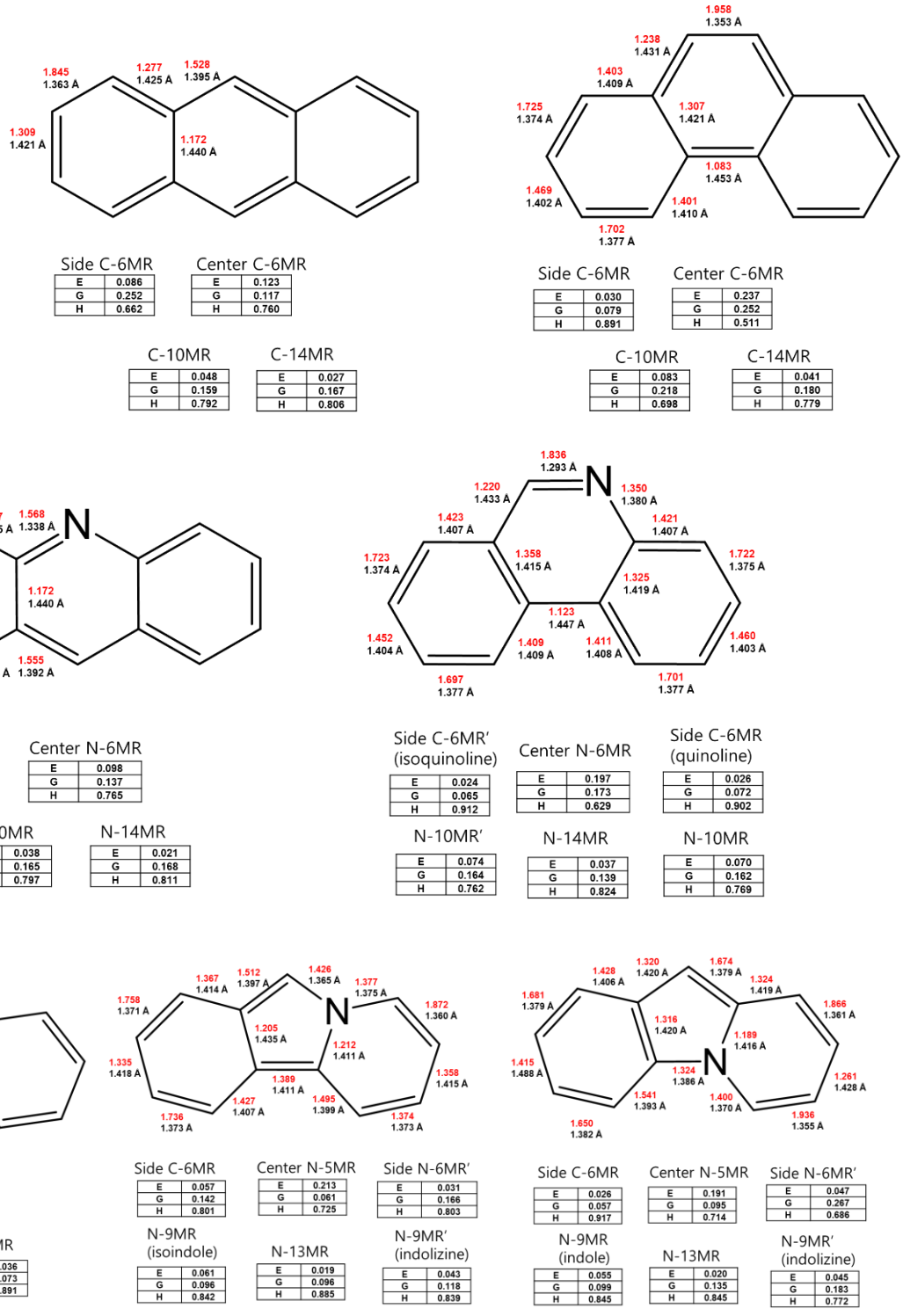


Figure S9. Bond lengths (black), Pauling bond numbers (red), and HOMA parameters of tricycles.

Optimized molecular structures (B3LYP/6-311G(2df,p))

1. Benzene

C	0.00000000	1.39029300	0.00000000
C	1.20402900	0.69514700	0.00000000
C	1.20402900	-0.69514700	0.00000000
C	0.00000000	-1.39029300	0.00000000
C	-1.20402900	-0.69514700	0.00000000
C	-1.20402900	0.69514700	0.00000000
H	0.00000000	2.47396700	0.00000000
H	2.14251800	1.23698300	0.00000000
H	2.14251800	-1.23698300	0.00000000
H	0.00000000	-2.47396700	0.00000000
H	-2.14251800	-1.23698300	0.00000000
H	-2.14251800	1.23698300	0.00000000

2. Pyridine

C	0.00000000	1.34663400	0.00000000
C	1.20338100	0.65109200	0.00000000
C	1.16549400	-0.73623900	0.00000000
C	-0.07105600	-1.36633200	0.00000000
C	-1.21608600	-0.57845000	0.00000000
N	-1.19443900	0.75449800	0.00000000
H	2.08157400	-1.31498200	0.00000000
H	-0.00486700	2.43267300	0.00000000
H	2.14424000	1.18748900	0.00000000
H	-0.15134500	-2.44637300	0.00000000
H	-2.19893400	-1.04053100	0.00000000

3. Pyrrole

C	0.00000000	1.12107100	0.33031700
C	0.00000000	0.71022800	-0.97944800
C	0.00000000	-0.71022800	-0.97944800
C	0.00000000	-1.12107100	0.33031700
N	0.00000000	0.00000000	1.11812300
H	0.00000000	0.00000000	2.12293700
H	0.00000000	2.10771300	0.76213100
H	0.00000000	1.35651300	-1.84224400
H	0.00000000	-1.35651300	-1.84224400
H	0.00000000	-2.10771300	0.76213100

4. Naphthalene

C	0.00000000	2.42309100	0.70569000
C	0.00000000	1.24048000	1.39682000
C	0.00000000	0.00000000	0.71401900
C	0.00000000	0.00000000	-0.71401900
C	0.00000000	1.24048000	-1.39682000
C	0.00000000	2.42309100	-0.70569000
H	0.00000000	-1.23905900	2.48130900
H	0.00000000	3.36521800	1.24076600
H	0.00000000	1.23905900	2.48130900
C	0.00000000	-1.24048000	1.39682000
C	0.00000000	-1.24048000	-1.39682000
H	0.00000000	1.23905900	-2.48130900
H	0.00000000	3.36521800	-1.24076600
C	0.00000000	-2.42309100	-0.70569000
C	0.00000000	-2.42309100	0.70569000
H	0.00000000	-1.23905900	-2.48130900
H	0.00000000	-3.36521800	-1.24076600
H	0.00000000	-3.36521800	1.24076600

5. Quinoline

C	2.38831100	-0.71426200	0.00000200
C	1.20213300	-1.39944600	0.00000100
C	-0.02855900	-0.70218100	0.00000000
C	-0.01403400	0.72426400	0.00000000
C	1.22800700	1.40189400	0.00000100
C	2.40290600	0.69781100	0.00000200
H	3.32658300	-1.25610300	0.00000300
H	1.16626700	-2.48144800	0.00000200
C	-1.26135500	1.38791800	-0.00000100
H	1.23447600	2.48648100	0.00000100
H	3.35067400	1.22252800	0.00000200
C	-2.41317500	0.65072500	-0.00000100
C	-2.31748300	-0.75897500	-0.00000300
H	-1.28927100	2.47223900	-0.00000100
H	-3.38696100	1.12432400	0.00000000
H	-3.22570400	-1.35656500	0.00000000
N	-1.18522400	-1.41970600	-0.00000100

6. Isoquinoline

C	-2.41813700	-0.58713700	0.00000000
C	-1.28463600	-1.35443100	0.00000000
C	-0.01877300	-0.72519700	0.00000000
C	0.00000000	0.69706000	0.00000000

C	-1.24760100	1.37033300	0.00000000
H	1.20252500	-2.50818700	0.00000000
H	-3.39912600	-1.05012800	0.00000000
H	-1.35328900	-2.43622600	0.00000000
C	1.21157000	-1.42415800	0.00000000
C	1.23833200	1.37864800	0.00000000
H	-1.25571600	2.45874700	0.00000000
C	2.41379700	0.67523400	0.00000000
C	2.39721900	-0.73710900	0.00000000
H	1.24241500	2.46300200	0.00000000
H	3.36255400	1.19787600	0.00000000
H	3.33556100	-1.27894100	0.00000000
N	-2.41222200	0.77062700	0.00000000

7. Indole

C	-0.24816200	0.74847600	0.00000800
C	-0.24691500	-0.67015000	-0.00004600
C	0.93216100	-1.41277000	0.00004800
C	2.12725900	-0.71564300	0.00019400
C	2.15048800	0.68906800	0.00024800
C	0.97942000	1.42327600	0.00015400
C	-1.62011900	1.16257700	-0.00004900
C	-2.38131900	0.03077600	-0.00032300
H	0.91688000	-2.49668100	0.00000200
H	3.06240200	-1.26255300	0.00027200
H	3.10522000	1.20111100	0.00037600
H	1.00910900	2.50684600	0.00022000
H	-1.99288800	2.17403100	0.00001500
H	-3.45326000	-0.08301600	-0.00049600
H	-1.87593800	-2.03152900	-0.00029500
N	-1.56120000	-1.07740900	-0.00021500

8. Isoindole

C	0.24975800	-0.72342300	0.00002000
C	0.24975800	0.72342300	-0.00005100
C	-0.98140900	1.42544500	0.00003300
C	-2.14718100	0.71267800	0.00018100
C	-2.14718100	-0.71267800	0.00024800
C	-0.98140900	-1.42544500	0.00016800
C	1.57818400	-1.13075800	-0.00004900
C	1.57818400	1.13075800	-0.00018600
H	-0.99433900	2.50950100	-0.00001000
H	-3.09699400	1.23441000	0.00025800

H	-3.09699400	-1.23440900	0.00037800
H	-0.99433800	-2.50950100	0.00023700
H	2.02421400	-2.11046300	-0.00001400
H	3.34843800	0.00000000	-0.00050300
H	2.02421500	2.11046300	-0.00026800
N	2.34193800	0.00000000	-0.00032400

9. Indolizine

C	0.27902100	0.74972500	-0.00005600
C	-0.96914100	1.40972900	0.00001700
C	-2.13062000	0.69311000	0.00015300
C	-2.08629900	-0.72937300	0.00022700
C	-0.89469100	-1.37699000	0.00016500
C	1.57390700	-1.10785100	-0.00002300
C	2.40225100	-0.00433300	-0.00039200
C	1.60723700	1.15523800	-0.00013000
H	-0.97692100	2.49239600	-0.00001600
H	-3.08736900	1.19875200	0.00022700
H	-2.99856600	-1.30988600	0.00035600
H	-0.79472000	-2.45345200	0.00023800
H	1.79676200	-2.16135400	0.00005800
H	3.48023600	-0.04208800	-0.00062300
H	1.94707100	2.17788900	-0.00015900
N	0.27764600	-0.66254200	0.00002200

10. Anthracene

C	0.00000000	3.64559900	0.71056700
C	0.00000000	2.47083400	1.40133700
C	0.00000000	1.21884400	0.71996700
C	0.00000000	1.21884400	-0.71996700
C	0.00000000	2.47083400	-1.40133700
C	0.00000000	3.64559900	-0.71056700
C	0.00000000	0.00000000	1.39819100
C	0.00000000	0.00000000	-1.39819100
C	0.00000000	-1.21884400	-0.71996700
C	0.00000000	-1.21884400	0.71996700
C	0.00000000	-2.47083400	1.40133700
H	0.00000000	-2.47008600	2.48570900
C	0.00000000	-3.64559900	0.71056700
C	0.00000000	-3.64559900	-0.71056700
C	0.00000000	-2.47083400	-1.40133700
H	0.00000000	0.00000000	2.48346900
H	0.00000000	4.58968600	1.24211600

H	0.00000000	2.47008600	2.48570900
H	0.00000000	2.47008600	-2.48570900
H	0.00000000	4.58968600	-1.24211600
H	0.00000000	0.00000000	-2.48346900
H	0.00000000	-4.58968600	1.24211600
H	0.00000000	-4.58968600	-1.24211600
H	0.00000000	-2.47008600	-2.48570900

11. Phenanthrene

C	0.00000000	3.54759100	-0.29495400
C	0.00000000	2.82699400	0.87505700
C	0.00000000	1.41772600	0.86247000
C	0.00000000	0.72671700	-0.37958200
C	0.00000000	1.49587600	-1.56077800
C	0.00000000	2.87194100	-1.52291900
C	0.00000000	0.67631100	2.08597900
C	0.00000000	-0.72671700	-0.37958200
C	0.00000000	-1.41772600	0.86247000
C	0.00000000	-0.67631100	2.08597900
C	0.00000000	-2.82699400	0.87505700
H	0.00000000	-3.33721400	1.83195700
C	0.00000000	-3.54759100	-0.29495400
C	0.00000000	-2.87194100	-1.52291900
C	0.00000000	-1.49587600	-1.56077800
H	0.00000000	1.22683700	3.02014900
H	0.00000000	4.63062600	-0.27086200
H	0.00000000	3.33721400	1.83195700
H	0.00000000	1.00466900	-2.52422700
H	0.00000000	3.43485200	-2.44866000
H	0.00000000	-1.22683700	3.02014900
H	0.00000000	-4.63062600	-0.27086200
H	0.00000000	-3.43485200	-2.44866000
H	0.00000000	-1.00466900	-2.52422700

12. Acridine

C	0.00000000	3.62639200	-0.65450300
C	0.00000000	2.47796300	-1.38792000
C	0.00000000	1.20718500	-0.74528100
C	0.00000000	1.15124600	0.69367800
C	0.00000000	2.37763900	1.42021500
C	0.00000000	3.57325800	0.76626000
C	0.00000000	0.00000000	-1.43818200
C	0.00000000	-1.15124600	0.69367800

C	0.00000000	-1.20718500	-0.74528100
C	0.00000000	-2.47796300	-1.38792000
H	0.00000000	-2.51318100	-2.47183900
C	0.00000000	-3.62639200	-0.65450300
C	0.00000000	-3.57325800	0.76626000
C	0.00000000	-2.37763900	1.42021500
H	0.00000000	0.00000000	-2.52390500
H	0.00000000	4.58957100	-1.15020000
H	0.00000000	2.51318100	-2.47183900
H	0.00000000	2.31415400	2.50081700
H	0.00000000	4.49903500	1.32932800
H	0.00000000	-4.58957100	-1.15020000
H	0.00000000	-4.49903500	1.32932800
H	0.00000000	-2.31415400	2.50081700
N	0.00000000	0.00000000	1.37534300

13. Phenanthridine

C	3.53032600	-0.24372300	-0.00000100
C	2.78556200	0.91164900	0.00012400
C	1.37931200	0.86058200	0.00000700
C	0.72062700	-0.39640000	-0.00010000
C	1.51083100	-1.56215400	-0.00026200
C	2.88547700	-1.48932600	-0.00022700
C	-0.72670400	-0.40373400	-0.00003700
C	-1.38575900	0.84825300	-0.00001100
C	-0.58824300	2.03908300	0.00002200
C	-2.79128200	0.91004900	0.00004800
H	-3.27310000	1.88151500	0.00005200
C	-3.53935700	-0.24295700	0.00009900
C	-2.89227700	-1.48839800	0.00012600
C	-1.51774600	-1.56917100	0.00006100
H	4.61247100	-0.19514200	0.00006800
H	3.24825900	1.89027800	0.00024800
H	1.03644300	-2.53489200	-0.00047400
H	3.47205700	-2.40013700	-0.00037400
H	-1.10261000	2.99972700	0.00011600
H	-4.62130500	-0.19574800	0.00014300
H	-3.48187300	-2.39746300	0.00021900
H	-1.04776400	-2.54346000	0.00013500
N	0.70468900	2.06468600	0.00011000

14. Carbazole

C	0.00000000	3.03344600	-1.14825600

C	0.00000000	3.41552500	0.19877300
C	0.00000000	2.47262600	1.21577400
C	0.00000000	1.12973500	0.85248400
C	0.00000000	0.72320300	-0.50378400
C	0.00000000	1.69408000	-1.50499200
H	0.00000000	3.79568300	-1.91755500
H	0.00000000	4.46868300	0.45302300
H	0.00000000	2.77500400	2.25648700
H	0.00000000	1.40608100	-2.54981600
C	0.00000000	-1.12973500	0.85248400
C	0.00000000	-2.47262600	1.21577400
C	0.00000000	-3.41552500	0.19877300
C	0.00000000	-3.03344600	-1.14825600
C	0.00000000	-1.69408000	-1.50499200
C	0.00000000	-0.72320300	-0.50378400
H	0.00000000	-2.77500400	2.25648700
H	0.00000000	-4.46868300	0.45302300
H	0.00000000	-3.79568300	-1.91755500
H	0.00000000	-1.40608100	-2.54981600
N	0.00000000	0.00000000	1.64884800
H	0.00000000	0.00000000	2.65379000

15. Isocarbazole

C	2.68601100	-1.79225500	0.00000000
C	1.81059100	-2.90758700	0.00000000
C	0.44848700	-2.75161500	0.00000000
C	-0.08752700	-1.44331800	0.00000000
C	0.80132700	-0.31631700	0.00000000
C	2.19442600	-0.51024000	0.00000000
H	3.75591000	-1.96086500	0.00000000
H	2.23443600	-3.90511400	0.00000000
H	-0.20751600	-3.61429300	0.00000000
H	2.87009200	0.33753300	0.00000000
C	-2.37286400	1.31198500	0.00000000
C	-2.11142600	2.64690600	0.00000000
C	-0.77915300	3.12346300	0.00000000
C	0.25461000	2.22044700	0.00000000
C	0.00000000	0.84518800	0.00000000
H	-3.36962100	0.89478200	0.00000000
H	-2.94415800	3.33734200	0.00000000
H	-0.58348700	4.18704700	0.00000000
H	1.28517500	2.55226800	0.00000000
H	-2.34305000	-1.47271700	0.00000000

C	-1.39725900	-0.95846900	0.00000000
N	-1.34015900	0.40498300	0.00000000

16. Pseudocarbazole

C	2.90068300	-1.20991700	0.00009400
C	3.39016400	0.13114000	0.00002500
C	2.52330900	1.18003200	-0.00003800
C	1.12205000	0.95468400	-0.00004400
C	1.56578200	-1.44023100	0.00007600
H	1.13253100	-2.42988500	0.00012100
C	-1.13604900	0.95025200	0.00000100
C	-2.51898000	1.20563000	0.00001100
C	-3.39928100	0.14463300	-0.00000100
C	-2.94254000	-1.18707200	-0.00002800
C	-1.59089500	-1.47452000	-0.00004500
C	-0.70155500	-0.40183500	-0.00001800
H	-2.88497500	2.22561800	0.00002100
H	-4.46613300	0.33421100	0.00000800
H	-3.66103100	-1.99725200	-0.00003800
H	-1.24540400	-2.50109000	-0.00006500
C	0.01647400	1.77943200	-0.00002200
N	0.68405600	-0.39191900	-0.00002600
H	0.04315200	2.85692200	-0.00005400
H	3.58279100	-2.04818200	0.00016700
H	2.87735100	2.20284700	-0.00007400
H	4.45835300	0.30687800	0.00003000