Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

for

Aromatic Nature of Neutral and Dianionic 1,4-diaza-2,3,5,6-tetraborinine Derivatives

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Methodology

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Fig. S1

Methodology

1. HOMA

The HOMA scheme for *N*-membered cyclic hydrocarbon compound is defined as shown in eq 1:

$$\mathrm{HOMA} = 1 - \frac{\alpha}{\mathrm{N}}\sum_i \left(\mathrm{R_{opt}} - R_i\right)^2 \quad (1)$$

In the equation, α is an empirical constant chosen to give a value of HOMA = 0 for a nonaromatic system and HOMA = 1 for aromatic system with all bonds equal to an optimal bond length (R_{opt}), N is the number of bonds taken into summation, Ri is an individual bond length and i represents the type of the bond. Krygowski and co-workers have proposed the extended HOMA scheme for heterocyclic compounds.

$$\mathrm{HOMA} = 1 - \left[257.7(1.388 - \mathrm{r_{av}})^2 + \frac{257.7}{\mathrm{N}}\sum_i (\mathrm{r_{av}} - r_i)^2\right] (2)$$

$$= 1 - \mathrm{EN} - \mathrm{GEO} \ (3)$$

where r_{av} and r_i are an average of C-C bond lengths and individual C-C bond lengths, respectively. To apply this scheme to the heterocyclic compounds, the Pauling concept of bond number n was introduced:

$$R(1) - \mathrm{R(n)} = c\ln(\mathrm{n}) \ (4)$$

$$\mathrm{n} = \exp\frac{\mathrm{R(1)-R(n)}}{\mathrm{c}} \ (5)$$

where R(n) and R(1) are the bond lengths whose bond numbers are n and 1, respectively. From reference value of R(1) and R(2), we can estimate the constant c for X-Y bond by using Eq.(5).

The R(1), R(2), and *c* values for CC, BB, and BN bonds listed in Table 1, have been recommended and were used herein for HOMA calculations. Using the bond number n, the X-Y bond length can be converted into the virtual C-C bond length (r_i) as

$$r_i = 1.467 - 0.1702 \ln(n) \quad (6)$$

Now we can evaluate HOMA value of various heterocyclic compounds by using Eq. (2).

Table 1. The R(1), R(2), and *c* values for CC, BB, and BN bonds.

	R(1)	R(2)	*c*
CC	1.467	1.349	0.1702
BB	1.647	1.526	0.1751
BN	1.564	1.363	0.2900

2. ELF

The electron localization function (ELF), introduced by Becke and Edgencombe, can be used to analyse the electronic localization and characteristics of a chemical bond. The value of ELF at which two basins merge is called a bifurcation value. The ring-closure bifurcation value is the value of ELF at which all basins in the ring merge to form one continuous cyclic basin. A separation of the ELF values into its σ and π components (namely, ELF_σ and ELF_π) was proposed as new aromaticity scales. Both ELF_σ and ELF_π are defined as the ELF values at the relative bifurcation points that is the (3, -1) critical points (CPs) of the ELF basin that only contribute from different molecular orbitals (π-orbitals or σ-orbitals). Aromatic molecules should hold at least the following two properties: (i) the maximal difference between the bifurcation values, ELF_π should be small, and (ii) the ELF_π should be above a certain threshold (0.64–0.70).[1] In this study, the aromaticity of the heterocyclic inorganic benzenes were also considered by averaged ELF_σ and ELF_π.[2]

3. PDI

The *para*-delocalization index (PDI), proposed by Sola and co-workers is derived from Bader's Atoms in Molecules (AIM) theory.[3] This index is defined as the average of three electron delocalization index (DIs) of *para*-related atoms in a given six-membered ring.[4-6] The higher PDI values, the more aromatic system is.

4. NICS

The computation of nucleus independent chemical shifts (NICSs): $NICS(1)_{zz}$, $NICS(0)_{\pi zz}$, and FiPC-NICS was used. Significantly negative (shielded) NICS values indicate a diatropic ring current and aromaticity, while positive (deshielded) values denote a paratropic ring current and antiaromaticity. The group of Pino-Rios and Tiznado remarked evaluating the s- and p-electron contributions to the out-of-plane components of NICS is the most adequate assessment for the quantitative analysis. The Tiznado and co-workers proposed a free of in-plane component NICS (FiPC-NICS) to assess aromaticity, identifying the point along the axis perpendicular to the molecular plane where the in-plane component of NICS becomes zero. It also allows visualizing the relation between the in-plane and out-of-plane components of NICS. The plots of these correlations provide curves whose shapes seem to be characteristics for aromatic, nonaromatic and antiaromatic systems. We also used the anisotropy of the current-induced density (ACID) to visualize ring current over the studied rings.

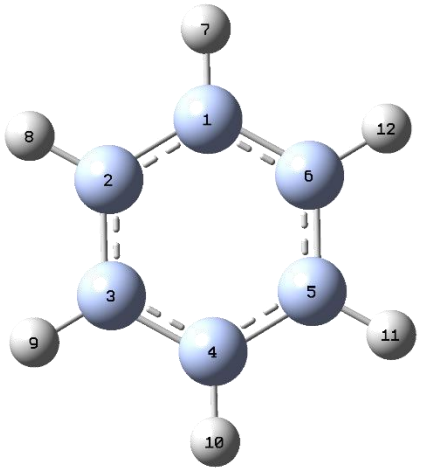
5. ASE

ASE has been evaluated using different isodesmic and homodesmotic (Scheme 1) reactions. The isodesmic reaction have been proposed for inorganic analogues. On the other hand, the

Tiznado and co-workers proposed the homodesmotic reaction to avoid sp^3 hybridization of boron atom, which is expected to generate strain in the B−H bonds.[7, 8] Here, we can evaluate ASE value of model compounds.

Table S1. Optimized structure of **1**, **2**, **3**, **3'**, and **4'** obtained by DFT calculations (atom, x-, y-, z-positions in Å).

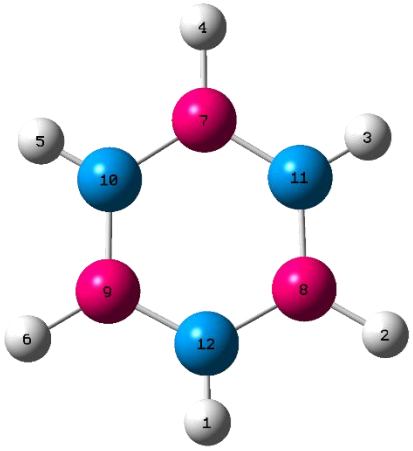
1:



C	-1.337282	-0.394667	0.000002
C	-0.326732	-1.355449	0.000062
C	1.010416	-0.960785	-0.000056
C	1.337249	0.394786	0.000007
C	0.326849	1.355419	0.000057
C	-1.010499	0.960699	-0.000052

H	-2.377180	-0.701703	-0.000061
H	-0.581008	-2.409500	0.000080
H	1.796302	-1.707800	-0.000122
H	2.377220	0.701555	0.000021
H	0.580872	2.409526	-0.000001
H	-1.796207	1.707909	-0.000038

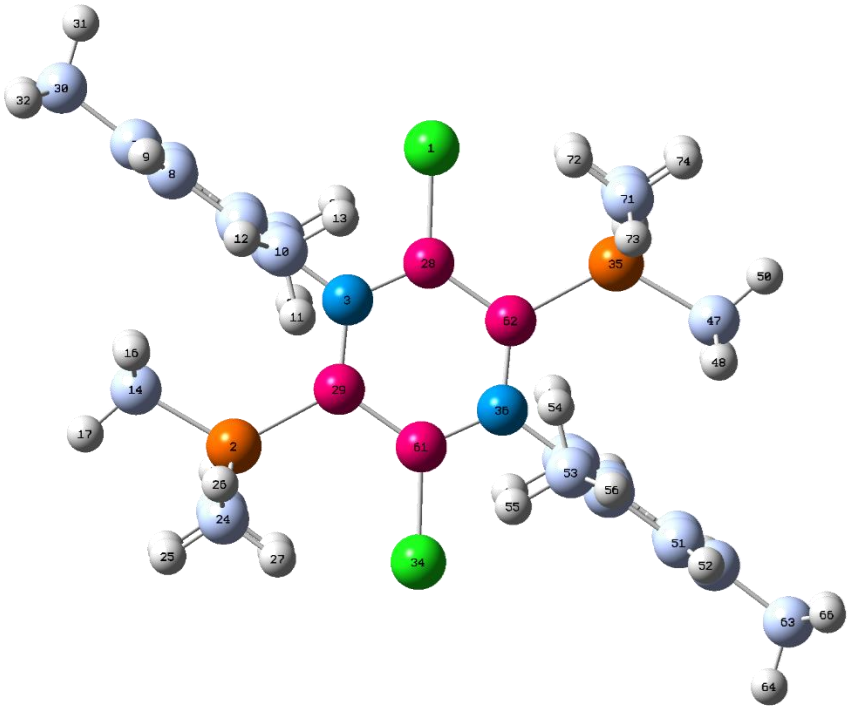
2:



B	1.107098	0.939067	-0.000001
B	0.259706	-1.428296	-0.000013
B	-1.366800	0.489237	0.000011
N	-0.252105	1.386574	-0.000012
N	1.326878	-0.474967	0.000009
N	-1.074774	-0.911613	-0.000001

H	-1.844157	-1.564238	-0.000002
H	0.472832	-2.600706	-0.000006
H	2.276761	-0.814952	0.000017
H	2.015871	1.709846	0.000017
H	-0.432620	2.379185	-0.000016
H	-2.488699	0.890870	0.000036

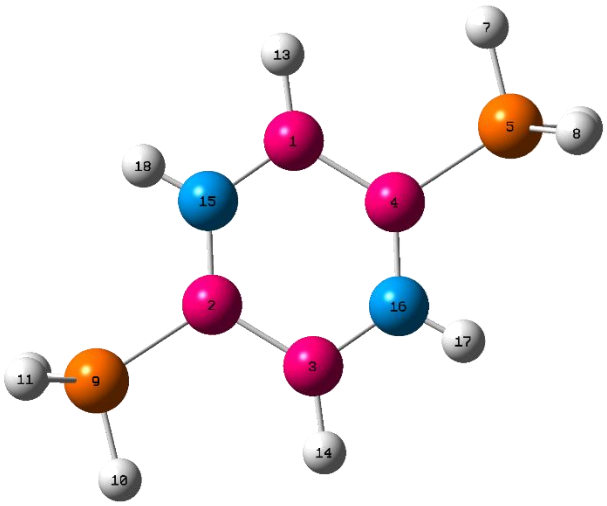
3:



Cl	1.443887	3.034615	-0.000316
P	2.074707	-2.734296	0.000166
N	1.525743	0.220088	0.000007
C	2.953580	0.448090	-0.000027
C	3.638188	0.571637	-1.219821
C	3.638169	0.572060	1.219728
C	5.732364	0.886061	-0.000087
C	5.020150	0.780271	-1.195624
H	5.550417	0.870728	-2.139647
C	2.903183	0.523746	-2.536999
H	2.197125	-0.309114	-2.582505
H	3.604289	0.437479	-3.369896
H	2.318105	1.437564	-2.680231
C	3.908169	-2.642620	0.000389
H	4.265469	-2.111609	0.881626
H	4.265653	-2.112009	-0.881021
H	4.307449	-3.660086	0.000652
C	5.020140	0.780681	1.195472
H	5.550400	0.871437	2.139471
C	2.903176	0.524628	2.536930
H	2.196737	-0.307899	2.582534
H	2.318535	1.438741	2.680091
H	3.604265	0.438131	3.369818
C	1.724883	-3.809655	-1.450930
H	2.247077	-4.765681	-1.356419
H	2.061385	-3.301556	-2.356273
H	0.651368	-3.980820	-1.518282
B	0.629450	1.352049	-0.000034
B	0.979599	-1.131259	0.000067
C	7.219589	1.150633	-0.000134
H	7.426659	2.226599	-0.000696
H	7.701455	0.726021	-0.884352
H	7.701337	0.726960	0.884596
Cl	-1.443771	-3.034662	-0.000005
P	-2.074758	2.734156	0.000116
N	-1.525674	-0.220099	0.000097
C	-2.953514	-0.448089	0.000018

C	-3.638197	-0.571850	1.219737
C	-3.638059	-0.571683	-1.219810
C	-5.732329	-0.885878	-0.000180
C	-5.020175	-0.780408	1.195411
H	-5.550500	-0.871028	2.139386
C	-2.903300	-0.524195	2.536985
H	-2.196713	0.308218	2.582382
H	-3.604438	-0.437315	3.369793
H	-2.318847	-1.438375	2.680472
C	-3.908216	2.642231	0.000284
H	-4.265620	2.111933	-0.881348
H	-4.265465	2.110847	0.881316
H	-4.307606	3.659656	0.000939
C	-5.020035	-0.780233	-1.195683
H	-5.550249	-0.870728	-2.139733
C	-2.902985	-0.524017	-2.536961
H	-2.196528	0.308505	-2.582381
H	-2.318335	-1.438104	-2.680251
H	-3.604023	-0.437366	-3.369876
C	-1.724780	3.809562	1.451123
H	-2.247057	4.765543	1.356634
H	-2.061119	3.301476	2.356536
H	-0.651272	3.980801	1.518344
B	-0.629391	-1.352063	0.000127
B	-0.979510	1.131238	0.000079
C	-7.219566	-1.150377	-0.000302
H	-7.426689	-2.226332	-0.001189
H	-7.701290	-0.726944	0.884555
H	-7.701414	-0.725477	-0.884394
C	1.724473	-3.809670	1.451143
H	2.060694	-3.301588	2.356599
H	0.650940	-3.980847	1.518169
H	2.246703	-4.765689	1.356763
C	-1.725060	3.809602	-1.450963
H	-0.651575	3.980992	-1.518244
H	-2.061382	3.301429	-2.356334
H	-2.247458	4.765523	-1.356501

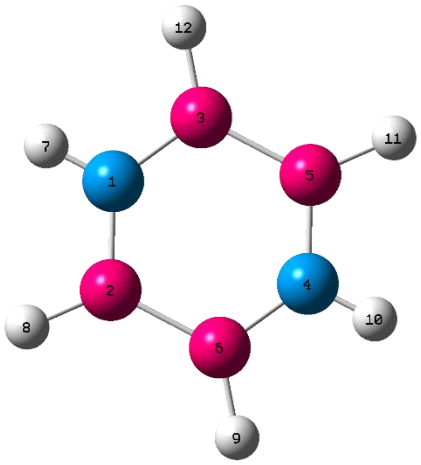
3’:



B	-0.689367	1.398504	-0.000123
B	1.446781	0.045569	-0.000050
B	0.689367	-1.398409	-0.000154
B	-1.446782	-0.045466	-0.000042
P	-3.356866	0.025883	0.000128
H	-4.135502	-0.515849	1.065419
H	-3.784547	1.362637	0.000207
H	-4.135919	-0.515770	-1.064910
P	3.356865	-0.025968	0.000032

H	3.784315	-1.362794	-0.000001
H	4.135799	0.515637	-1.065110
H	4.135801	0.515571	1.065210
H	-1.172566	2.499066	0.000112
H	1.172597	-2.498958	-0.000283
N	0.753049	1.301630	-0.000028
N	-0.753042	-1.301537	-0.000127
H	-1.267176	-2.175714	-0.000174
H	1.267175	2.175811	0.000067

4':



N	1.476540	0.000000	0.000002
B	0.828160	-1.306783	-0.010984
B	0.828162	1.306782	0.011048
N	-1.476540	0.000002	-0.000019
B	-0.828153	1.306794	0.011677
B	-0.828155	-1.306793	-0.011660

H	2.492346	-0.000002	-0.000031
H	1.592312	-2.268909	0.032669
H	-1.592339	-2.268979	0.031682
H	-2.492368	0.000001	-0.000040
H	-1.592334	2.268976	-0.031805
H	1.592315	2.268900	-0.032763

Table S2. Calculated NICS values (ppm) of **4'** at different level.

	NICS		$NICS_{zz}$		$NICS_{\pi zz}$	
Distance (Å)	0	1	0	1	0	1
6-311g+(d,p)	7.70	2.33	-5.68	-15.42	-20.73	-17.02
6-311g+(2df,2pd)	8.07	1.79	-6.71	-16.38	-21.41	-17.93
6-311g+(3df,3dp)	7.79	1.34	-4.94	-14.75	-19.96	-16.00

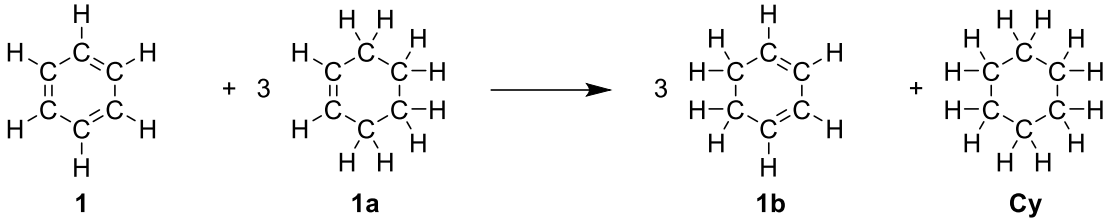
Table S3. Calculated HOMA values of studied molecules.

	Type	Bond length	bond number
1	C-C	1.39439	1.532
	C-C	1.39418	1.534
	C-C	1.39441	1.532
	C-C	1.39417	1.534
	C-C	1.39438	1.532
	C-C	1.39420	1.534
2	B-N	1.43101	1.582
	B-N	1.43098	1.582
	B-N	1.43101	1.582
	B-N	1.43096	1.582
	B-N	1.43100	1.582
	B-N	1.43098	1.582
3	B-B	1.62407	1.143
	B-B	1.62404	1.143
	B-N	1.45754	1.444
	B-N	1.44384	1.513
	B-N	1.45753	1.444
	B-N	1.44384	1.513
3'	B-B	1.63056	1.101
	B-B	1.63057	1.101
	B-N	1.43492	1.561
	B-N	1.44566	1.504
	B-N	1.43491	1.561
	B-N	1.44567	1.504
4'	B-B	1.65632	0.950
	B-B	1.65632	0.950
	B-N	1.45885	1.437
	B-N	1.45885	1.437
	B-N	1.45883	1.437
	B-N	1.45883	1.437

Table S4. Properties of electron density at ring critical point of **1-4'**.

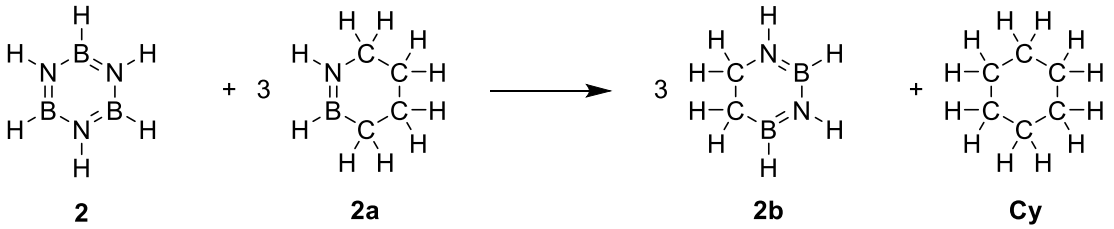
	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$H(r_c)$	λ_1	λ_2	λ_3	ε
1	0.0215	0.1614	0.0326	0.0078	-0.0168	0.0891	0.0891	-1.1886
2	0.0197	0.1195	0.0251	0.0047	-0.0140	0.0668	0.0668	-1.2100
3	0.0171	0.0785	0.0171	0.0025	-0.0108	0.0346	0.0546	-1.3104
3'	0.0172	0.0850	0.0184	0.0029	-0.0113	0.0417	0.0546	-1.2708
4'	0.0156	0.0821	0.0174	0.0031	-0.0096	0.0453	0.0464	-1.2110

Table S5. Raw energy data for RSE calculation of (a).



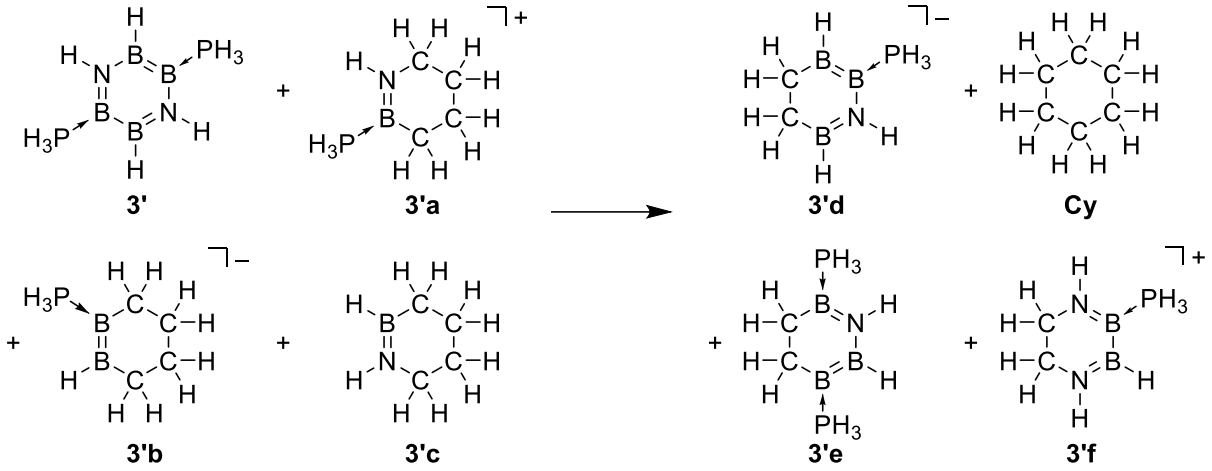
(a)	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Gibbs Free Energy	Sum of electronic and zero-point Energies	Sum of electronic and thermal Energies	Sum of electronic and thermal Enthalpies	Sum of electronic and thermal Free Energies
1	0.100153	0.104553	0.105497	0.072688	-232.211089	-232.206689	-232.205745	-232.238554
1a	0.14558	0.151103	0.152048	0.116929	-234.567577	-234.562053	-234.561109	-234.596227
1b	0.121786	0.126971	0.127916	0.093549	-233.362089	-233.356904	-233.35596	-233.390326
Cy	0.169491	0.175223	0.176168	0.141737	-235.775335	-235.769602	-235.768658	-235.803089
RSE [au]								0.053168
RSE [kcal mol^{-1}]								33.36292

Table S6. Raw energy data for RSE calculation of (b).



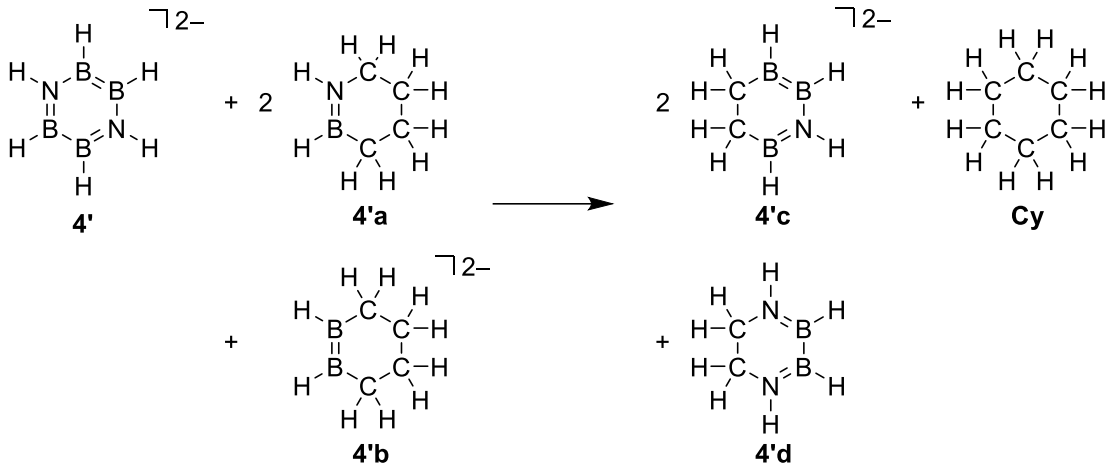
(b)	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Gibbs Free Energy	Sum of electronic and zero-point Energies	Sum of electronic and thermal Energies	Sum of electronic and thermal Enthalpies	Sum of electronic and thermal Free Energies
2	0.093176	0.098388	0.099333	0.065051	-242.655345	-242.650133	-242.649189	-242.68347
2a	0.14289	0.148729	0.149673	0.113981	-238.02607	-238.020231	-238.019287	-238.054979
2b	0.11703	0.122837	0.123781	0.088211	-240.314275	-240.308469	-240.307524	-240.343095
Cy	0.169491	0.175223	0.176168	0.141737	-235.775335	-235.769602	-235.768658	-235.803089
RSE [au]								0.016033
RSE [kcal mol^{-1}]								10.0607075

Table S7. Raw energy data for RSE calculation of (c).



(c)	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Gibbs Free Energy	Sum of electronic and zero-point Energies	Sum of electronic and thermal Energies	Sum of electronic and thermal Enthalpies	Sum of electronic and thermal Free Energies
3'	0.123163	0.133732	0.134676	0.087362	-897.661346	-897.650776	-897.649832	-897.697147
3'a	0.162639	0.171086	0.17203	0.129642	-580.344718	-580.336271	-580.335326	-580.377715
3'b	0.14289	0.148729	0.149673	0.113981	-238.02607	-238.020231	-238.019287	-238.054979
3'c	0.151726	0.160224	0.161169	0.119034	-550.613642	-550.605144	-550.6042	-550.646334
3'd	0.125097	0.133662	0.134606	0.092361	-552.891209	-552.882645	-552.881701	-552.923945
3'e	0.146388	0.157479	0.158423	0.109679	-895.368798	-895.357707	-895.356763	-895.405507
3'f	0.137604	0.145877	0.146821	0.104905	-582.572987	-582.564714	-582.56377	-582.605686
Cy	0.169491	0.175223	0.176168	0.141737	-235.775335	-235.769602	-235.768658	-235.803089
RSE [au]								0.037948
RSE [kcal mol-1]								23.81237

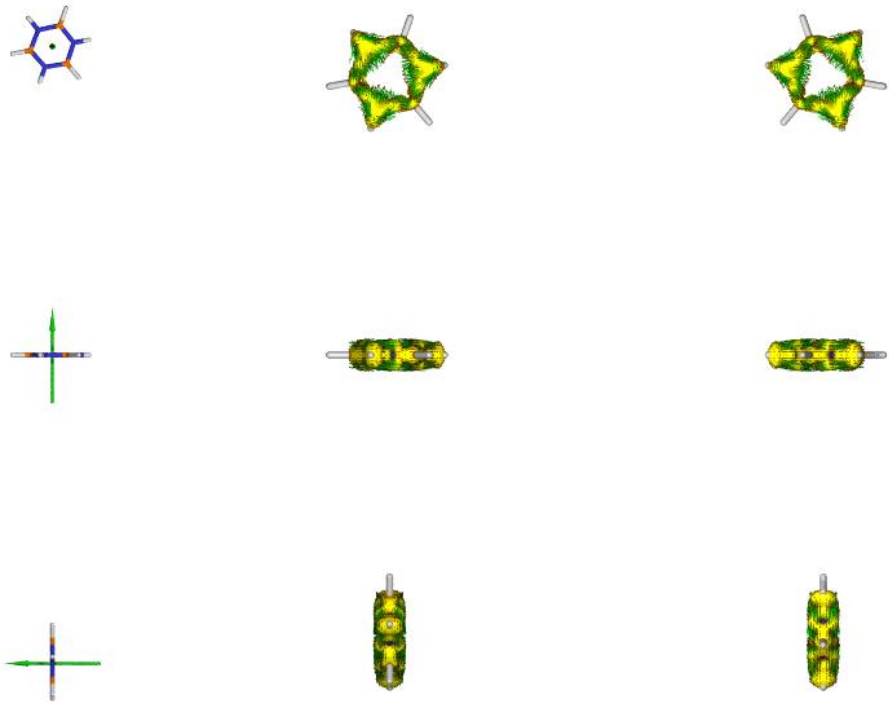
Table S8. Raw energy data for RSE calculation of (d).



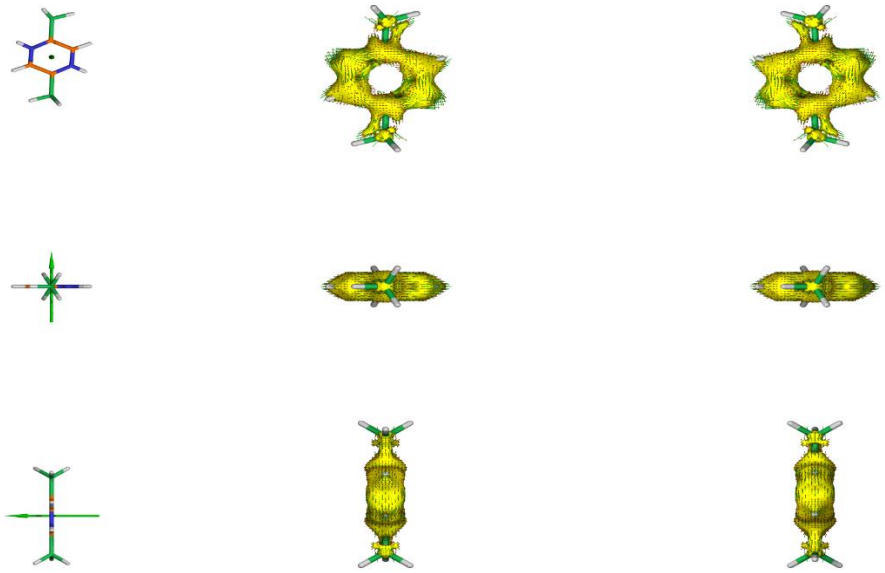
(d)	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Gibbs Free Energy	Sum of electronic and zero-point Energies	Sum of electronic and thermal Energies	Sum of electronic and thermal Enthalpies	Sum of electronic and thermal Free Energies
4'	0.081778	0.087475	0.08842	0.053433	-212.502999	-212.497301	-212.496357	-212.531343
4'a	0.14289	0.148729	0.149673	0.113981	-238.02607	-238.020231	-238.019287	-238.054979
4'b	0.130619	0.137045	0.137989	0.101362	-207.915235	-207.908809	-207.907865	-207.944492
4'c	0.106233	0.112401	0.113345	0.077334	-210.215626	-210.209458	-210.208514	-210.244525
4'd	0.117573	0.123267	0.124211	0.088945	-240.247536	-240.241842	-240.240897	-240.276163
Cy	0.169491	0.175223	0.176168	0.141737	-235.775335	-235.769602	-235.768658	-235.803089
RSE [au]								0.017491
RSE [kcal mol-1]								10.9756025

(**1**)

(**2**)



(**3'**)



(**4'**)

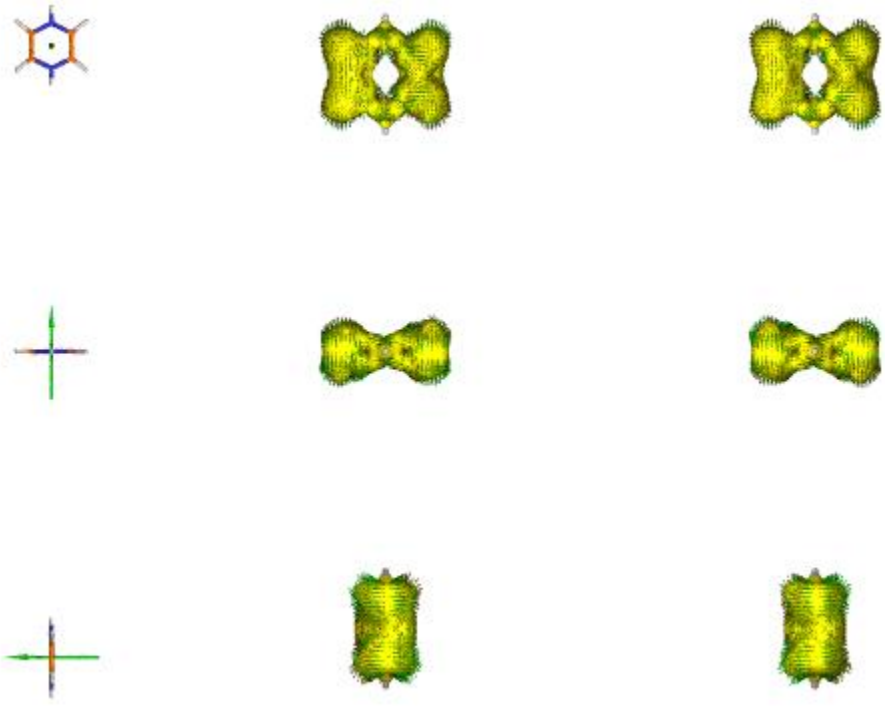


Figure S1. ACID plot of selected π orbitals at an isosurface value of 0.03.

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