Supporting Information

A theoretical study on the strain energy of helicene-containing carbon nanobelts

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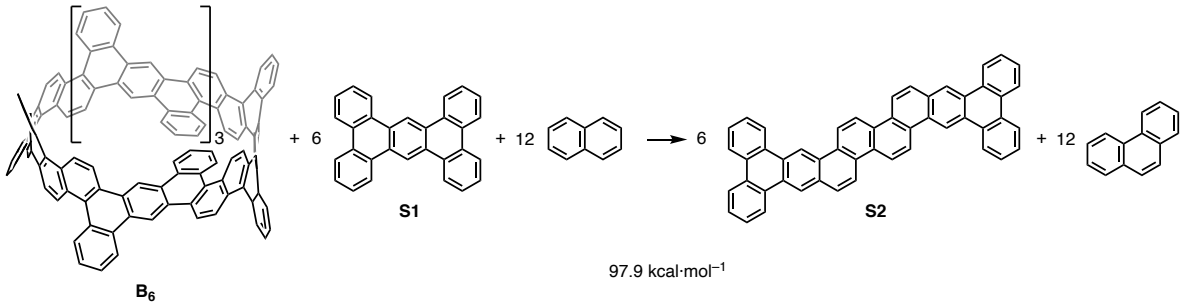
1. Methods of DFT study

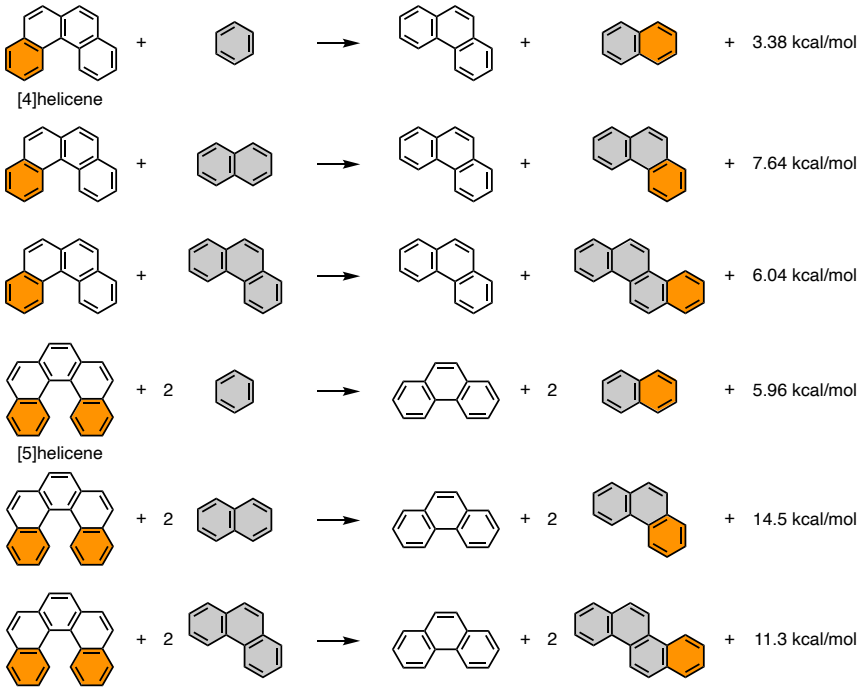
The Gaussian 16 program[S1] running on a NEC LX 110Rh system was used for optimization. B3LYP/6-31G(d))[S2,S3] level of theory was used unless otherwise noted. Structures were optimized without any symmetry assumptions. Plots and regression lines were drawn by Microsoft® Excel for Mac version 16.16.27. SEs per carbon atom were SE values divided by total number of carbon atoms.

2. Hypothetical reactions

Scheme S1. A hypothetical homodesmotic reaction for $\mathbf{B_6}$.

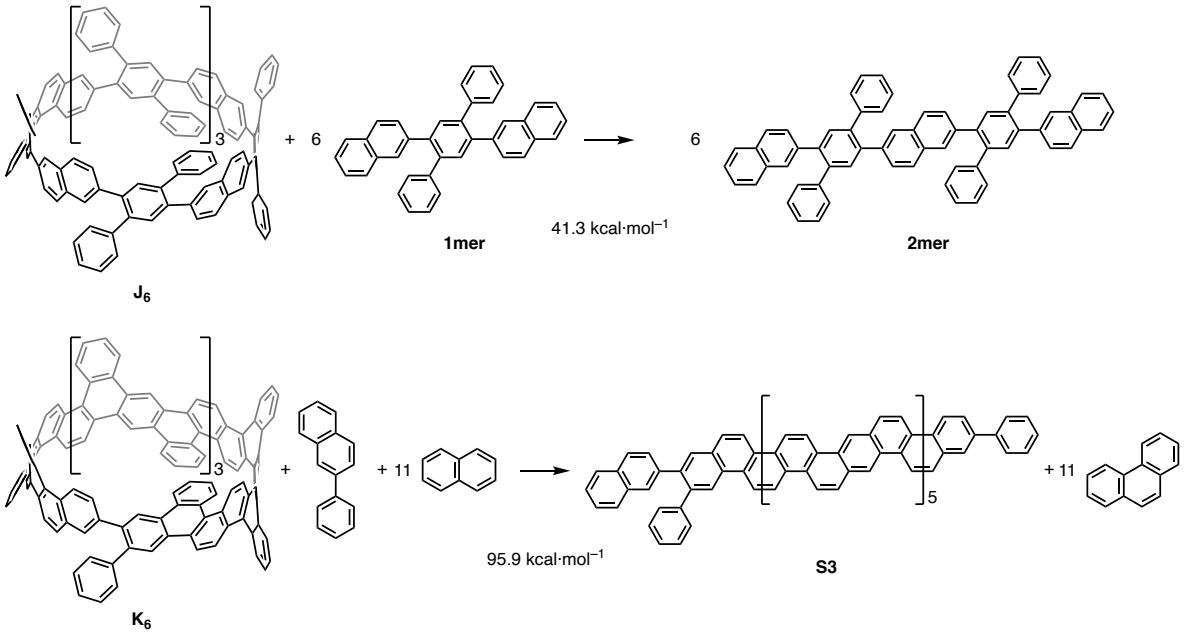


Scheme S2. Hypothetical homodesmotic reactions for [4]- and [5]helicenes.[a]

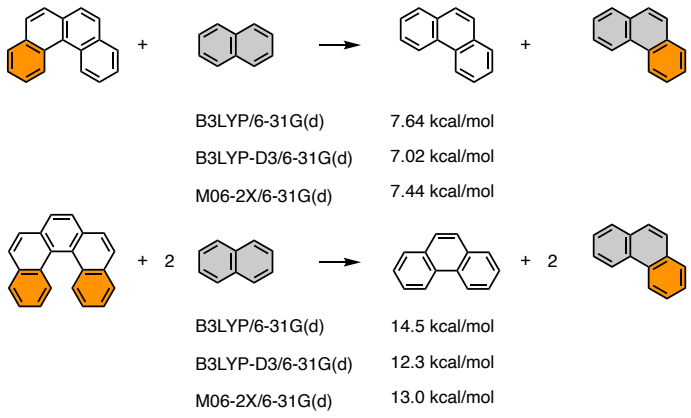


[a] According to these results and previous works,[24,25] SEs are dependent on the choice of reference molecules, and are underestimated when benzene/naphthalene is used. Also, using large π-conjugated molecules such as chrysene may cause underestimation. To avoid such problem, we chose phenanthrene and naphthalene as reference molecules in this work.

Scheme S3. Hypothetical homodesmotic reactions for J_6 and K_6.



Scheme S4. SEs of [4]- and [5]helicenes calculated by B3LYP/6-31G(d), B3LYP-D3/6-31G(d),[S4] and M06-2X/6-31G(d)[S5] level of theory.[a]



[a] According to these results and previous works,[25] SEs of [4]- and [5]helicenes are slightly underestimated when B3LYP-D3 or M06-2X level of theory is used.

3. Strain energies of CNBs

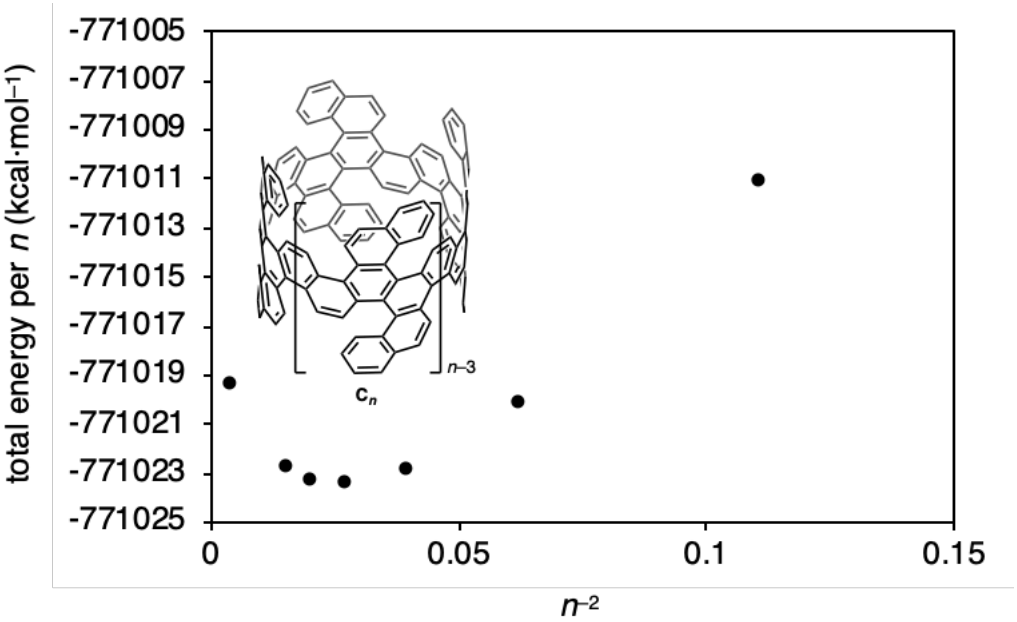


Fig. S1 Plot of the total energy per n of $\mathbf{C}_n$ versus n^{-2}.

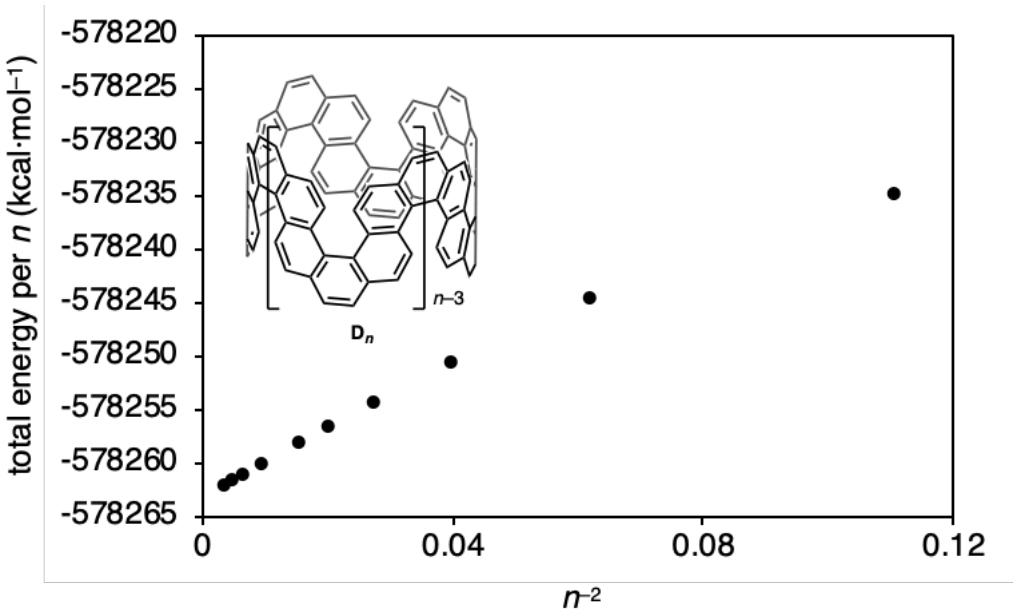


Fig. S2 Plot of the total energy per n of $\mathbf{D}_n$ versus n^{-2}.

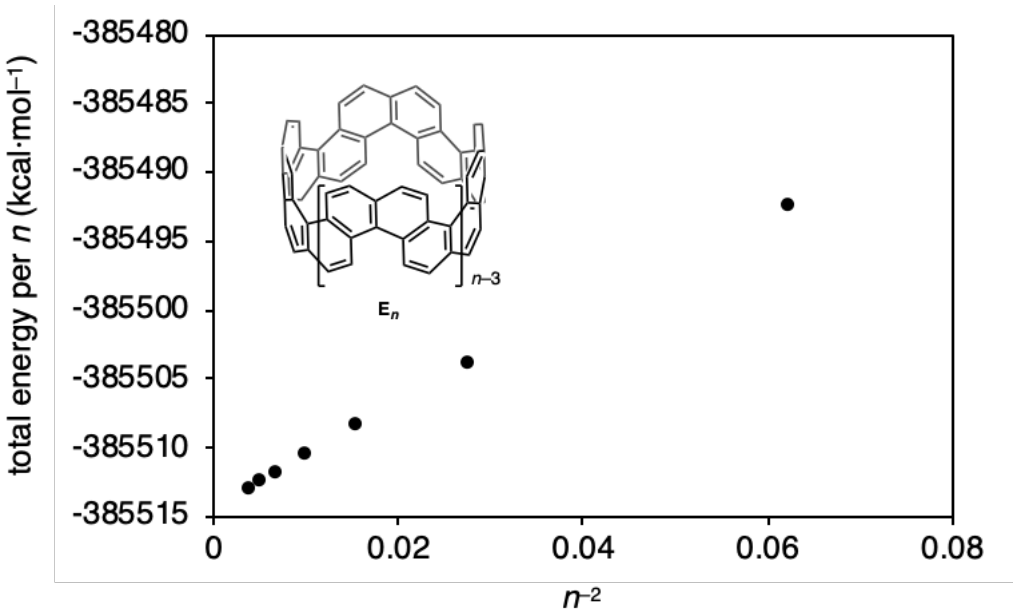


Fig. S3 Plot of the total energy per n of $\mathbf{E}_n$ versus n^{-2}.

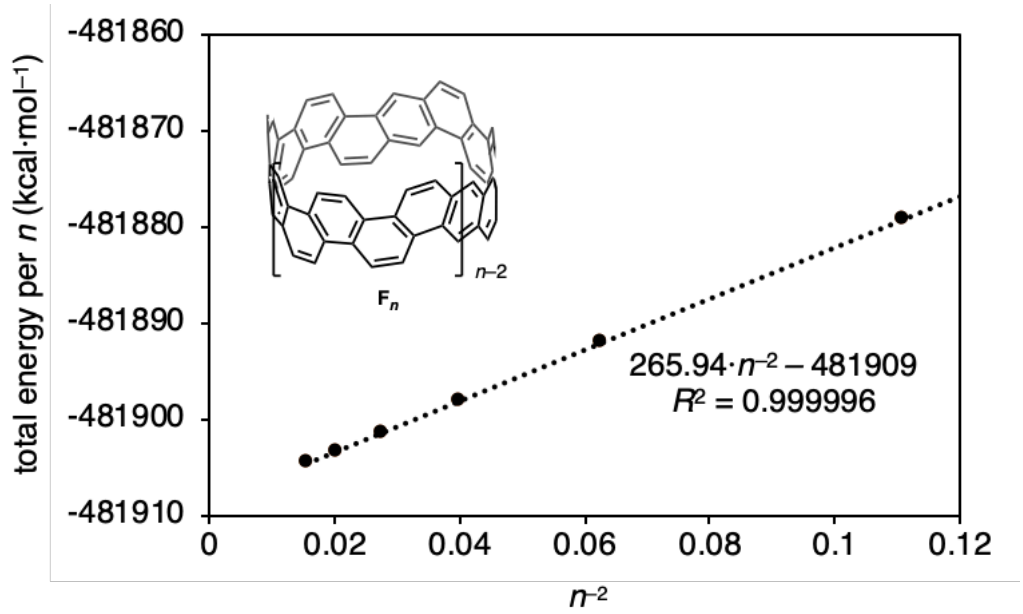


Fig. S4 Plot of the total energy per n of $\mathbf{F}_n$ versus n^{-2} with the linear regression line.

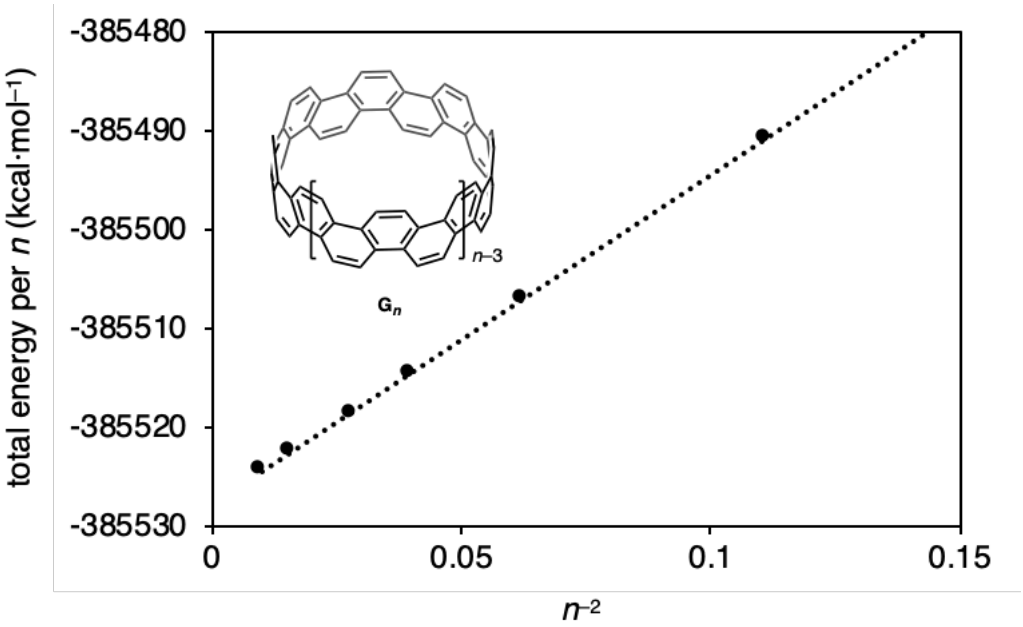


Fig. S5 Plot of the total energy per n of $\mathbf{G}_n$ versus n^{-2} with the linear regression line.

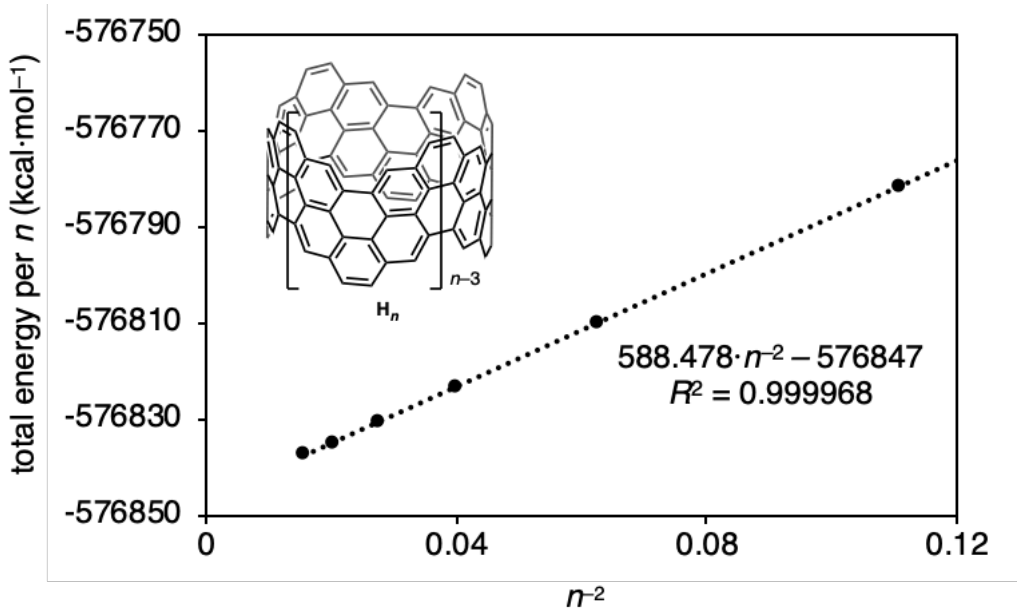


Fig. S6 Plot of the total energy per n of $\mathbf{H}_n$ versus n^{-2} with the linear regression line.

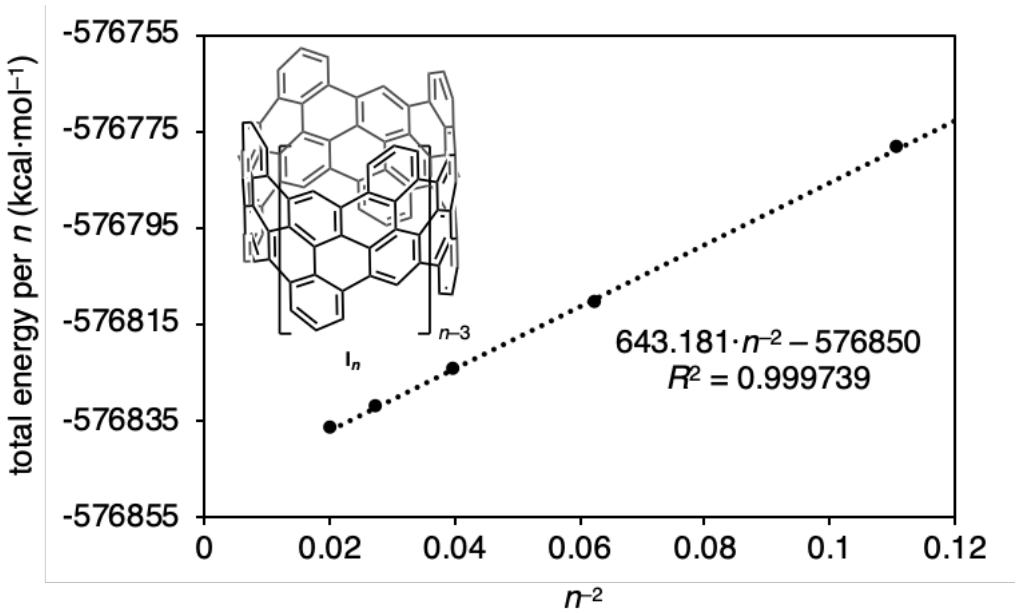


Fig. S7 Plot of the total energy per n of $\mathbf{I}_n$ versus n^{-2} with the linear regression line.

Table S1 SE and diameter of $\mathbf{A}_n$.

n	SE (kcal·mol^{-1})	diameter (Å)	SE per carbon atom (kcal·mol^{-1})
4	86.93	11.07	1.358
5	69.54	13.82	0.869
6	57.95	16.57	0.604
8	43.46	22.07	0.340
10	34.77	27.58	0.217
12	28.98	33.09	0.151
16	21.73	44.12	0.085

Table S2 SE and diameter of $\mathbf{B}_n$.

n	SE (kcal·mol^{-1})	diameter (Å)	SE per carbon atom (kcal·mol^{-1})
4	85.91	13.87	0.767
5	90.15	17.32	0.644
6	99.10	20.77	0.590
7	110.73	24.22	0.565
8	123.98	27.67	0.553
9	138.30	31.12	0.549
10	153.31	34.58	0.548
12	184.89	41.48	0.550
14	217.55	48.38	0.555

Table S3 SE and diameter of $\mathbf{C}_n$.

n	SE (kcal·mol^{-1})	diameter (Å)	SE per carbon atom (kcal·mol^{-1})
3	146.24	8.35	1.523
4	158.84	11.04	1.241
5	185.14	13.73	1.157
6	218.60	16.44	1.139
7	256.22	19.15	1.144
8	296.53	21.86	1.158
15	607.49	40.87	1.266

Table S4 SE and diameter of $\mathbf{D}_n$.

n	SE (kcal·mol^{-1})	diameter (Å)	SE per carbon atom (kcal·mol^{-1})
3	178.23	9.11	2.475
4	198.11	12.00	2.064
5	218.05	14.88	1.817
6	239.90	17.77	1.666
7	263.71	20.68	1.570
8	288.95	23.59	1.505
10	342.58	29.37	1.427
12	398.78	35.22	1.385
14	456.48	41.08	1.359
16	515.28	46.93	1.342

Table S5 SE and diameter of $\mathbf{E}_n$.

n	SE (kcal·mol^{-1})	diameter (Å)	SE per carbon atom (kcal·mol^{-1})
4	156.03	9.70	2.438
6	165.05	14.36	1.719
8	183.80	19.10	1.436
10	208.03	23.86	1.300
12	235.31	28.63	1.226
14	264.39	33.39	1.180
16	294.65	38.16	1.151

4. Energy values of optimized structures

Table S6 Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree).[a]

	E	*E* + *ZPE*	*H*	*G*
A_4	2458.16344407	-2457.41707	-2457.37559	-2457.48243
A_5	-3072.76872158	-3071.83458	-3071.78218	-3071.91234
A_6	-3687.36459936	-3686.24284	-3686.17949	-3686.33321
A_8	-4916.54208781	-4915.04546	-4914.96015	-4915.16193
A_{10}	-6145.71018037	-6143.83872	-6143.73151	-6143.98126
A_{12}	-7374.87336311	-7372.62735	-7372.49816	-7372.79782
A_{16}	-9833.19263837	-9830.19755	-9830.02447	-9830.42133
B_4	-4301.90284889	-4300.59021	-4300.51607	-4300.69328
B_5	-5377.40768833	-5375.76600	-5375.67280	-5375.89104
B_6	-6452.90479112	-6450.93432	-6450.82202	-6451.08185
B_7	-7528.39759911	-7526.09836	-7525.96698	-7526.26853
B_8	-8603.88773146	-8601.25982	-8601.10934	-8601.45283
B_9	-9679.37614114	-9676.41958	-9676.25000	-9676.63565
B_{10}	-10754.8633519	-10751.57825	-10751.38956	-10751.81460
B_{12}	-12905.8354408	-12901.89309	-12901.66620	-12902.17643
B_{14}	-15056.8055839	-15052.20627	-15051.94112	-15052.53656
C_3	-3687.24115994	-3686.11878	-3686.05541	-3686.20892
C_4	-4916.38170334	-4914.88330	-4914.79847	-4914.99661
C_5	-6145.49983807	-6143.62601	-6143.51968	-6143.76299
C_6	-7374.60637126	-7372.35730	-7372.22950	-7372.51576
C_7	-8603.70605681	-8601.08200	-8600.93268	-8601.26454
C_8	-9832.80154418	-9829.80240	-9829.63159	-9830.00908
C_{15}	-18436.4220478	-18430.79945	-18430.47798	-18431.17933
D_3	-2765.31562521	-2764.47695	-2764.42991	-2764.55049
D_4	-3687.15261318	-3686.03306	-3685.96986	-3686.12538
D_5	-4608.98963340	-4607.58878	-4607.50971	-4607.69680
D_6	-5530.82347353	-5529.14145	-5529.04650	-5529.26854
D_7	-6452.65414403	-6450.69105	-6450.58019	-6450.83421
D_8	-7374.48240468	-7372.23843	-7372.11159	-7372.40161
D_{10}	-9218.13394438	-9215.32818	-9215.16939	-9215.52747
D_{12}	-11061.7813084	-11058.41387	-11058.22308	-11058.64845

D_{14}	-12905.4261809	-12901.49720	-12901.27439	-12901.77080
D_{16}	-14749.0694553	-14744.57877	-14744.32393	-14744.88778
E_4	-2458.07505018	-2457.32758	-2457.28600	-2457.39560
E_6	-3687.22671318	-3686.10189	-3686.03943	-3686.19259
E_8	-4916.36229160	-4914.86098	-4914.77736	-4914.97571
E_{10}	-6145.48895017	-6143.61139	-6143.50655	-6143.75054
E_{12}	-7374.61062988	-7372.35699	-7372.23088	-7372.52106
E_{14}	-8603.72938382	-8601.09972	-8600.95233	-8601.28883
E_{16}	-9832.84622777	-9829.84061	-9829.67192	-9830.05505
F_3	-2304.50939012	-2303.80942	-2303.77062	-2303.87261
F_4	-3072.76452803	-3071.82966	-3071.77709	-3071.90852
F_5	-3841.00518688	-3839.83579	-3839.76936	-3839.93101
F_6	-4609.23849230	-4607.83464	-4607.75434	-4607.94638
F_7	-5377.46754074	-5375.82941	-5375.73522	-5375.95805
F_8	-6145.69397097	-6143.82155	-6143.71346	-6143.96728
G_3	-1843.54505190	-1842.98644	-1842.95571	-1843.04168
G_4	-2458.16723784	-2457.42024	-2457.37852	-2457.48799
G_5	-3072.77082219	-3071.83587	-3071.78303	-3071.91389
G_6	-3687.36516815	-3686.24239	-3686.17841	-3686.33658
G_8	-4916.53999678	-4915.04197	-4914.95561	-4915.16160
G_{10}	-6145.70561216	-6143.83260	-6143.72382	-6143.97881
H_3	-2758.23020855	-2757.52056	-2757.48079	-2757.58157
H_4	-3677.82772811	-3676.87917	-3676.82530	-3676.95406
H_5	-4597.39224497	-4596.20526	-4596.13720	-4596.29454
H_6	-5516.94024832	-5515.51504	-5515.43275	-5515.61915
H_7	-6436.47890919	-6434.81556	-6434.71903	-6434.93478
H_8	-7356.01185300	-7354.11032	-7353.99958	-7354.24197
I_3	-2758.21642259	-2757.50484	-2757.46529	-2757.56539
I_4	-3677.82955897	-3676.87808	-3676.82455	-3676.95184
I_5	-4597.40365656	-4596.21289	-4596.14524	-4596.30043
I_6	-5516.95788503	-5515.52806	-5515.44623	-5515.62974
I_7	-6436.50052734	-6434.83174	-6434.73569	-6434.94790
J_6	-6467.09536833	-6464.87595	-6464.74661	-6465.06300
1mer	-1463.75343199	-1463.23547	-1463.20599	-1463.29727

2mer	-2541.61426228	-2540.72625	-2540.67488	-2540.81835
benzene	-232.253750536	-232.15303	-232.14770	-232.18049
naphthalene	-385.892706628	-385.74491	-385.73717	-385.77611
phenanthrene	-539.538630394	-539.34380	-539.33342	-539.37865
chrysene	-693.181978362	-692.94025	-692.92714	-692.97877
[4]helicene	-693.172469823	-692.93042	-692.91751	-692.96836
[5]helicene	-846.806915776	-846.51845	-846.50286	-846.55951
bp	-845.654380392	-845.38700	-845.37259	-845.42641
K_6	-6454.08520730	-6452.09360	-6451.98000	-6452.24406
2-phenylnaphthalene	-616.950161806	-616.72132	-616.70890	-616.75941
S1	-1154.11224810	-1153.73017	-1153.70844	-1153.78145
S2	-1922.33093428	-1921.71463	-1921.67911	-1921.78357
S3	-5381.08491677	-5379.38323	-5379.28382	-5379.53559
B3LYP-D3/6-31G(d)				
[4]helicene	-693.198150102	-692.95598	-692.94308	-692.99393
[5]helicene	-846.841948084	-846.55322	-846.53765	-846.59426
naphthalene	-385.903979145	-385.75611	-385.74837	-385.78730
phenanthrene	-539.556629780	-539.36169	-539.35131	-539.39655
M06-2X/6-31G(d)				
[4]helicene	-692.879090504	-692.63455	-692.62171	-692.67241
[5]helicene	-846.455678177	-846.16417	-846.14868	-846.20512
naphthalene	-385.718805919	-385.56950	-385.56179	-385.60069
phenanthrene	-539.304797723	-539.10802	-539.09768	-539.14287

a) E: electronic energy; ZPE: zero-point energy; H (= $E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT$): sum of electronic and thermal enthalpies; G (= $H - TS$): sum of electronic and thermal free energies.

5. References

S1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision B.01, Gaussian, Inc., Wallingford CT, 2016.

S2 A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652.

S3 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785-789.

S4 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

S5 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.