

Supplementary information

Oxidation-induced double aromaticity in *periodo-*polycyclic hydrocarbons

Sladana Đorđević,¹ Jordi Poater,² Miquel Solà,^{3*} Slavko Radenković^{1*}

¹*University of Kragujevac, Faculty of Science, P. O. Box 60, 34000 Kragujevac, Serbia*

²*Departament de Química Inorgànica i Orgànica & IQTCUB, Universitat de Barcelona, 08028 Barcelona, Spain; ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain*

³*Institut de Química Computacional i Catalisi and Departament de Química, Universitat de Girona, 17003 Girona, Catalonia, Spain*

*Corresponding authors: slavkoradenkovic@kg.ac.rs; miquel.sola@udg.edu

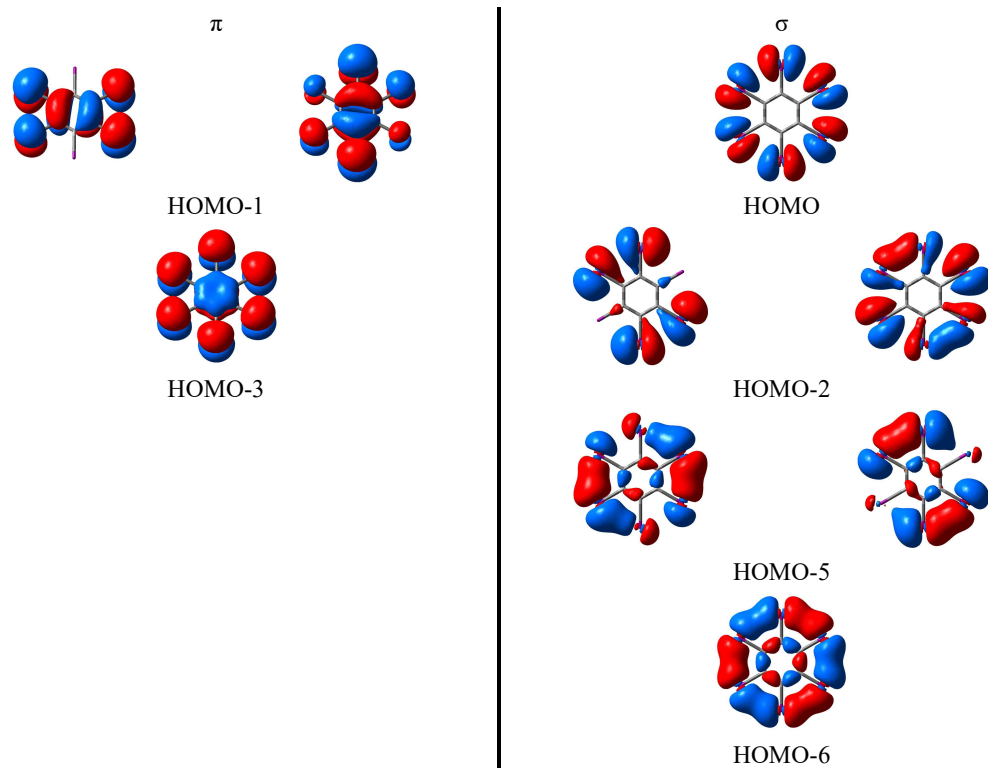


Figure S1. Relevant σ - and π -molecular occupied orbitals in C_6I_6 .

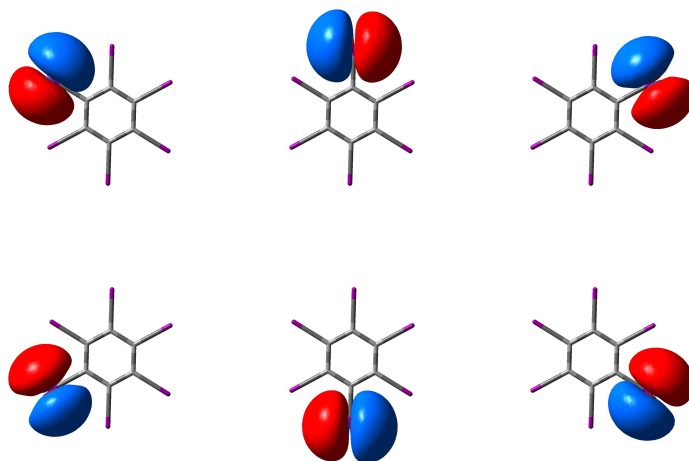


Figure S2. In-plane lone pair PNBs on the iodine atoms in C₆I₆ (isovalue is 0.02e) obtained from NBO analysis at the B3LYP/def2-TZVP level of theory.

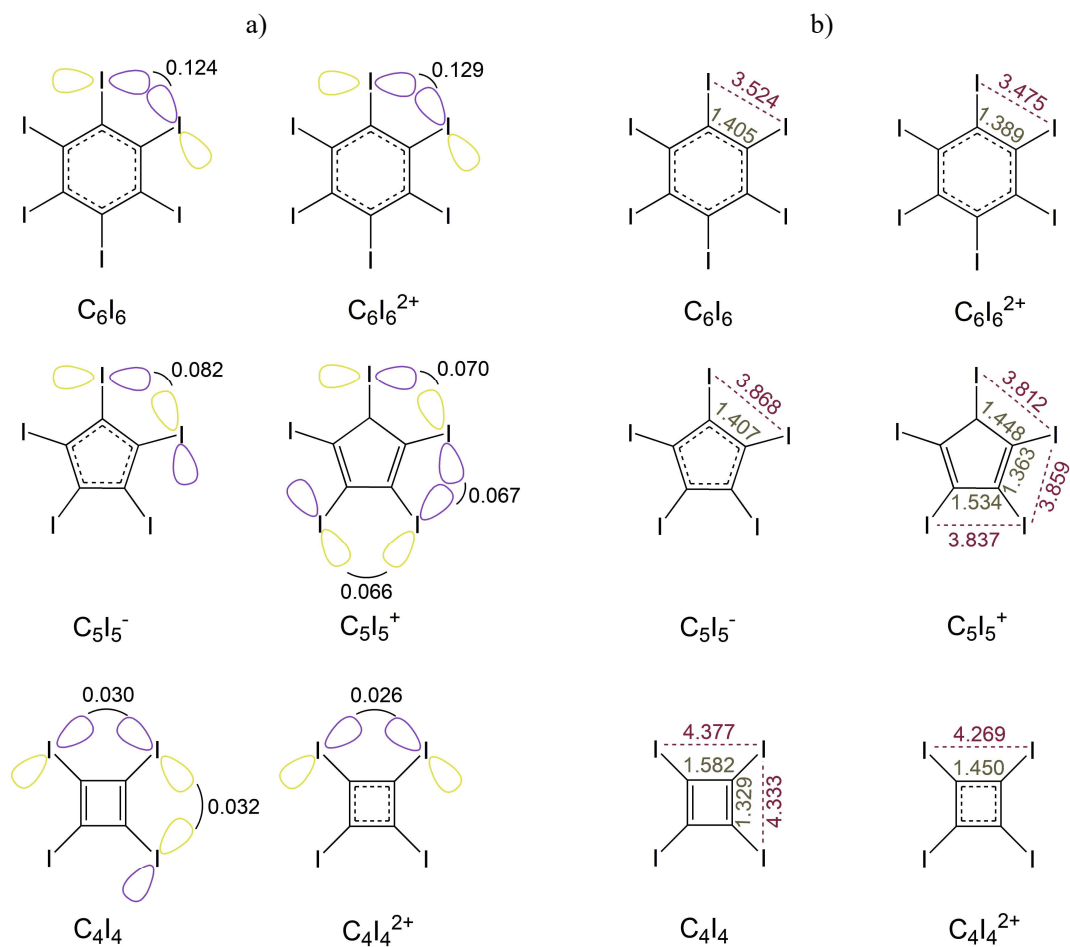


Figure S3. The absolute values of the overlap integral of in-plane lone pair PNBOs (a) and the C–C and I–I distances (in Å) for symmetry-unique bonds (b) in C_6I_6 , $C_6I_6^{2+}$, $C_5I_5^-$, $C_5I_5^+$, C_4I_4 , and $C_4I_4^{2+}$.

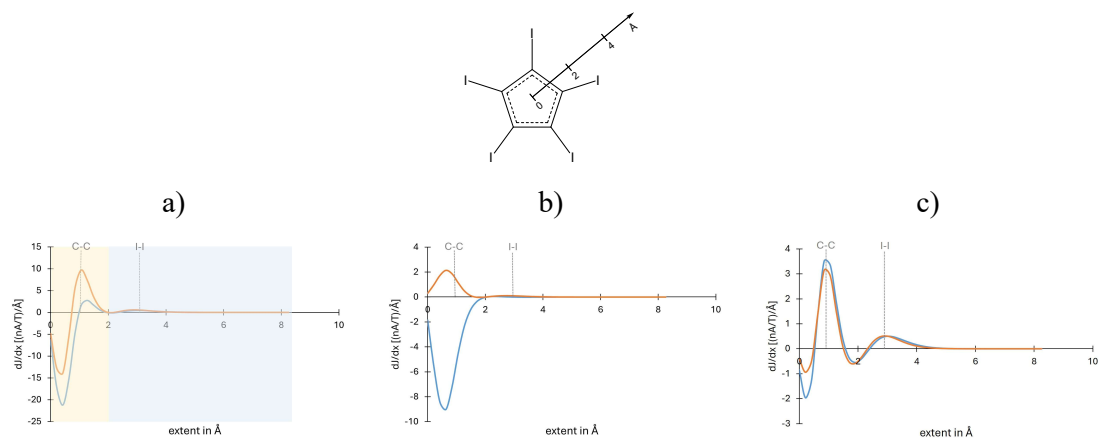


Figure S4. Total (a), π (b) and σ (c) bond current strengths profiles of $C_5I_5^-$ (blue line) and $C_5I_5^+$ (orange line).

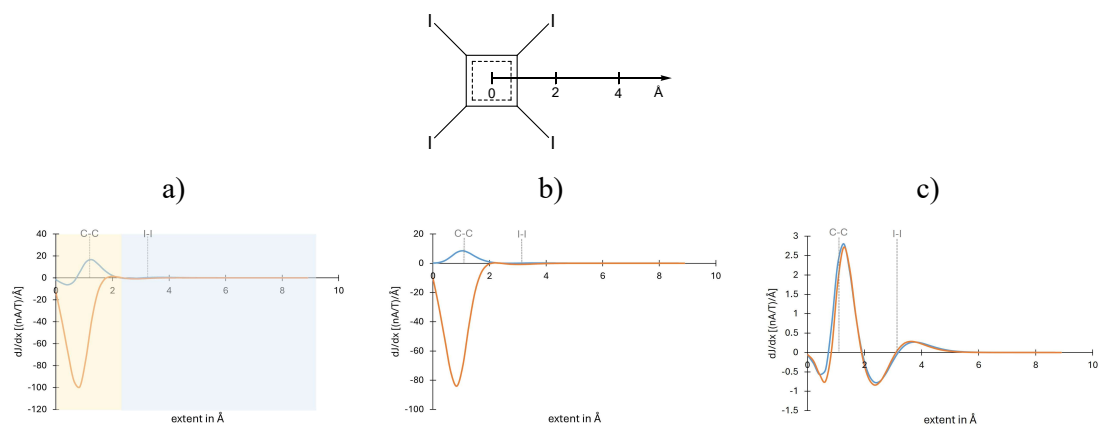
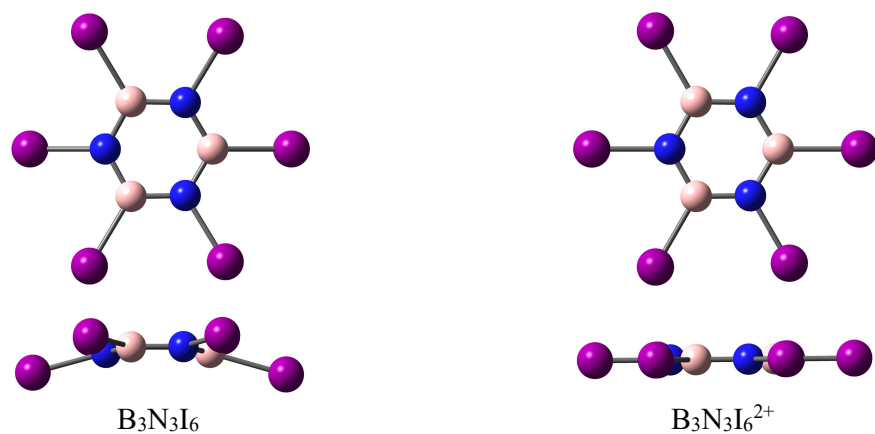


Figure S5. Total (a), π (b) and σ (c) bond current strengths profiles of C_4I_4 (blue line) and $C_4I_4^{2+}$ (orange line).

a)



b)

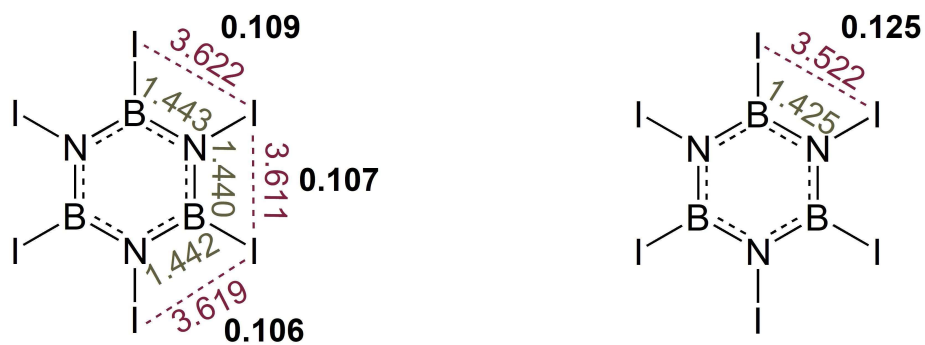
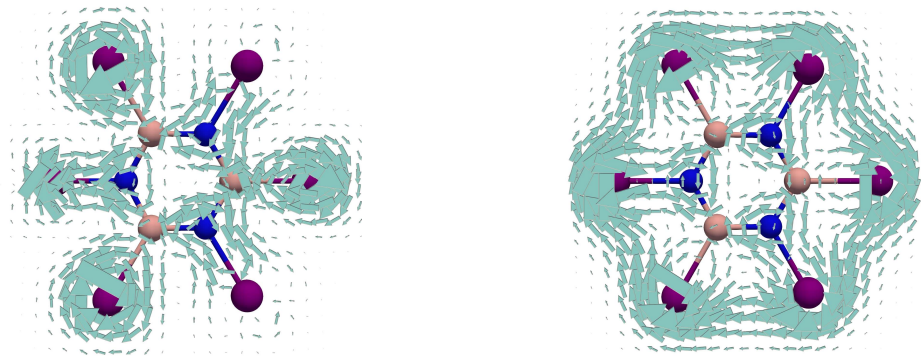


Figure S6. a) Top and side views of optimized structures for $B_3N_3I_6$ (left) and $B_3N_3I_6^{2+}$ (right); b) The absolute values of the overlap integral values of halogen in-plane lone pair PNBOs (bold numbers), along with the B-N and I-I distances (in Å) for symmetry-unique bonds in $B_3N_3I_6$ (left) and $B_3N_3I_6^{2+}$ (right).

a)



b)

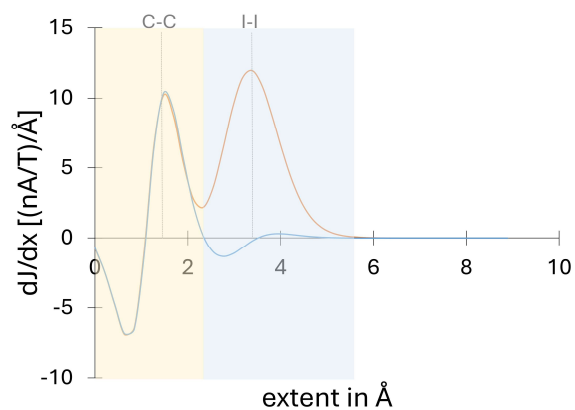
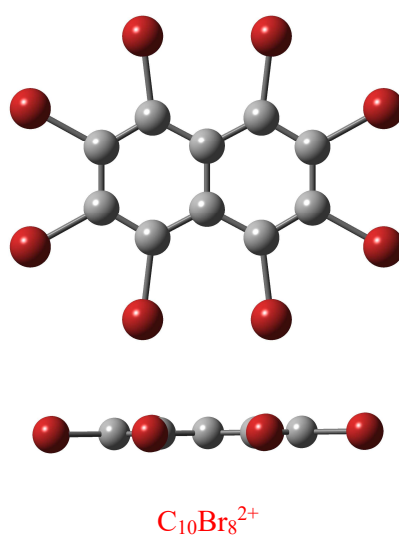
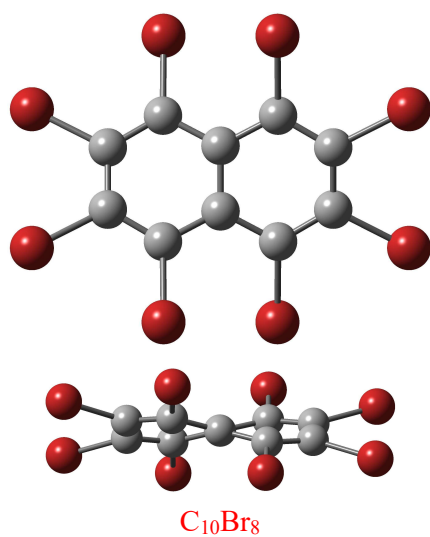


Figure S7. a) Total current density maps plotted 1 Bohr above the molecular plane of $B_3N_3I_6$ (left) and $B_3N_3I_6^{2+}$ (right); note that the neutral $B_3N_3I_6$ is nonplanar and apparent asymmetry in its current density distribution arises from technical limitations in visualizing current densities in nonplanar systems. b) Profiles of total bond current strengths for $B_3N_3I_6$ (blue line) and $B_3N_3I_6^{2+}$ (orange line).

a)



b)

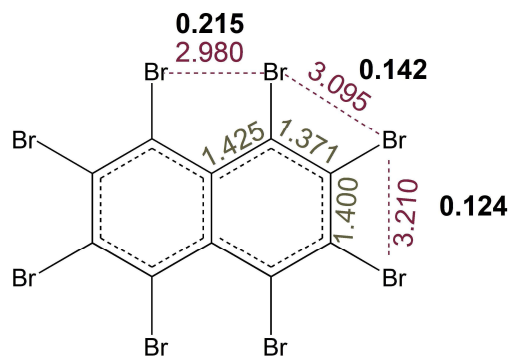
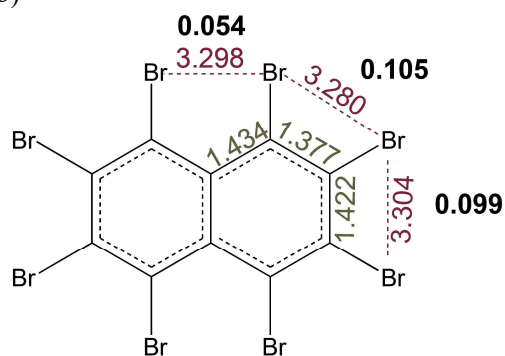
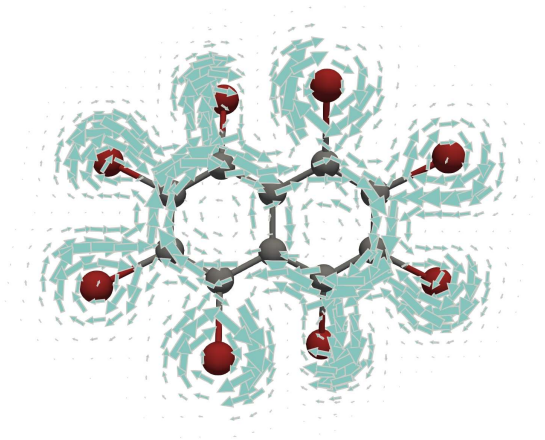


Figure S8. a) Top and side views of optimized structures for $C_{10}Br_8$ (left) and $C_{10}Br_8^{2+}$ (right); b) The absolute values of the overlap integral values of halogen in-plane lone pair PNBOs (bold numbers), along with the C–C and Br–Br distances (in Å) for symmetry-unique bonds in $C_{10}Br_8$ (left) and $C_{10}Br_8^{2+}$ (right).

a)



b)

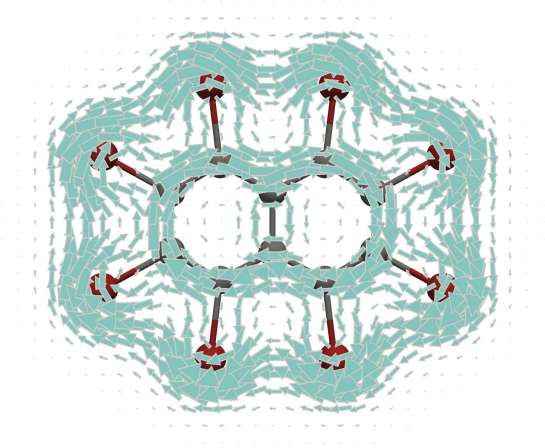


Figure S9. Total current density maps plotted 1 Bohr above the molecular plane of C₁₀Br₈ (a) and C₁₀Br₈²⁺ (b).

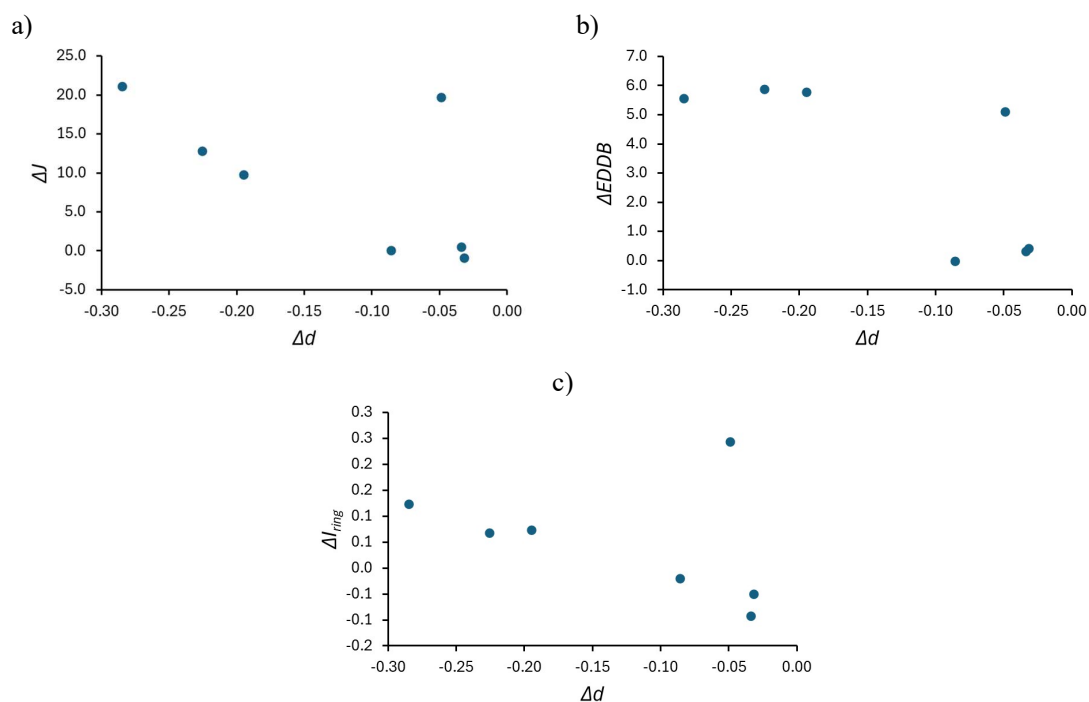


Figure S10. Correlation between the difference in average I-I distances (Δd , in Å) and the change in aromaticity indices between the neutral and the oxidized forms of the molecules examined. The $\text{C}_6\text{I}_6/\text{C}_6\text{I}_6^{2+}$ pair is a clear outlier.

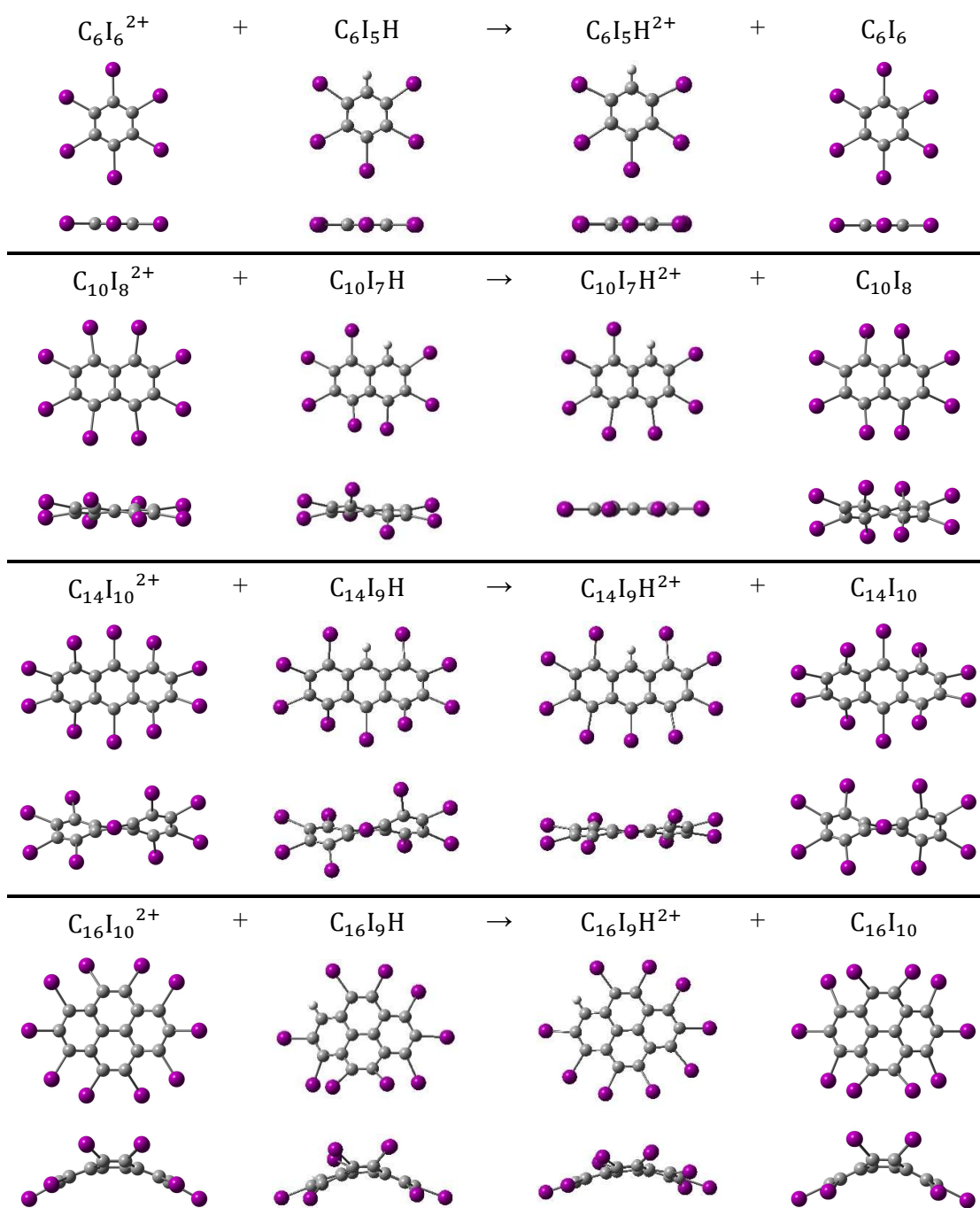


Figure S11. Homodesmotic reactions listed in Table 4, used to evaluate the aromatic stabilization energies of the examined compounds.

Table S1. The HOMO energy and the energies of the highest (E_H) and lowest (E_L) occupied σ -type molecular orbitals, as well as their difference (ΔE), all given in au.

molecule	E_{HOMO}	σ -MOs		
		E_H	E_L	ΔE
C_6I_6	-0.2213	-0.2213 (HOMO)	-0.3249 (HOMO-7)	0.1036
$C_5I_5^-$	-0.0715	-0.1176 (HOMO-1)	-0.1625 (HOMO-5)	0.0448
C_4I_4	-0.2087	-0.2788 (HOMO-2)	-0.2933 (HOMO-4)	0.0145

Table S2. Bond current strengths (J , in nA T⁻¹), EDDB (in a.u.), and I_{ring} (in a.u.) values for $C_6I_6^{2+}$ obtained using different density functionals and basis sets.

method	I_{ring}		EDDB _F		J [nA T ⁻¹]	
	C_6	I_6	C_6	I_6	C_6	I_6
B3LYP/def2-TZVP	0.624	0.310	5.038	5.333	8.6	18.7
B3LYP/def2-SVP	0.625	0.315	5.033	5.375	8.1	15.7
B3LYP/def2-TZVPPD	0.624	0.314	5.019	5.303	8.6	19.0
CAM-B3LYP/def2-TZVP	0.628	0.309	5.068	5.320	9.1	20.4
wB97xd/def2-TZVP	0.627	0.308	5.047	5.310	9.1	20.8
BP86/def2-TZVP	0.618	0.307	4.969	5.329	7.9	18.0

Table S3. Bond current strengths (J , in nA T⁻¹), EDDB (in a.u.), and I_{ring} (in a.u.) values for $B_3N_3I_6$ and $B_3N_3I_6^{2+}$.

		J [nA T ⁻¹]	EDDB _F	I_{ring}
$B_3N_3I_6$	B_3N_3	1.9	3.685	0.480
	I_6	-0.1	0.151	-0.057
$B_3N_3I_6^{2+}$	B_3N_3	1.8	3.871	0.487
	I_6	17.6	5.209	0.306

Table S4. Bond current strengths (J , in nA T⁻¹), EDDB (in a.u.), and I_{ring} (in a.u.) values for $C_{10}Br_8$ and $C_{10}Br_8^{2+}$.

		J [nA T ⁻¹]	EDDB _F	I_{ring}
$C_{10}Br_8$	C_{10}	8.6	6.216	0.578
	I_8	0.7	0.174	0.064
$C_{10}Br_8^{2+}$	C_{10}	10.4	7.123	0.589
	I_8	15.1	5.772	0.231

Table S5. Cartesian coordinates (in Å) of the optimized geometries for studied molecules obtained at the B3LYP/def2-TZVP level of theory.

C₆I₆				C₆I₆²⁺			
0 1				2 1			
C	-0.84633000	1.12139200	-0.00003300	C	-0.76824000	1.15787400	0.00000000
C	0.54788900	1.29349000	-0.00003300	C	0.61847900	1.24443800	0.00000000
C	1.39403800	0.17212800	-0.00003400	C	1.38650600	0.08651200	0.00000000
C	0.84632400	-1.12139600	-0.00003300	C	0.76823800	-1.15787400	0.00000000
C	-0.54788200	-1.29349300	-0.00003300	C	-0.61847800	-1.24443800	0.00000000
C	-1.39403900	-0.17212100	-0.00003300	C	-1.38650600	-0.08651100	0.00000000
I	2.12382700	-2.81222300	0.00000600	I	1.92201600	-2.89457200	0.00000000
I	-1.37543000	-3.24441400	0.00000300	I	-1.54773700	-3.11079900	0.00000000
I	-3.49709400	-0.43180900	0.00000400	I	-3.46764800	-0.21591200	0.00000000
I	-2.12388800	2.81217700	0.00000400	I	-1.92201500	2.89457300	0.00000000
I	1.37550000	3.24438500	0.00000500	I	1.54773700	3.11079900	0.00000000
I	3.49708400	0.43188300	0.00000100	I	3.46764700	0.21591000	0.00000000
C₅I₅⁻				C₅I₅⁺			
-1 1				1 1			
C	-1.17157000	0.24682200	-0.00000100	C	0.76892300	0.94862300	0.00000100
C	-0.12759800	1.19042700	0.00000000	C	1.19253000	-0.34641400	0.00000000
C	-0.59667500	-1.03756000	0.00000000	C	-0.76521400	0.95119100	0.00000000
C	0.80239500	-0.88772700	0.00000000	C	-1.19363700	-0.34256600	-0.00000100
C	1.09237800	0.48927000	-0.00000100	C	-0.00224000	-1.16554400	-0.00000100
I	-1.63967500	-2.85280500	0.00000100	I	-1.91393500	2.62696800	0.00000100
I	2.20650800	-2.44058100	0.00000000	I	-3.14934900	-1.02890800	-0.00000200
I	-3.22037700	0.67752900	-0.00000100	I	1.92327300	2.62088500	0.00000300
I	-0.35039100	3.27222700	0.00000100	I	3.14571400	-1.03998800	0.00000100
I	3.00405700	1.34349100	0.00000000	I	-0.00574300	-3.18408300	-0.00000200
C₄I₄				C₄I₄²⁺			
0 1				2 1			
C	0.79083000	0.66497800	-0.00050500	C	0.00000000	1.02503100	0.00005200
C	0.79164500	-0.66400100	-0.00041100	C	-1.02503000	0.00000000	-0.00005300
C	-0.79085700	-0.66495300	-0.00010800	C	0.00000000	-1.02503100	0.00005200
C	-0.79165800	0.66400600	-0.00019100	C	1.02503000	0.00000000	-0.00005300
I	-2.18998000	2.16508300	-0.00023500	I	3.01843400	0.00000000	-0.00024100
I	2.18712400	2.16788000	0.00030600	I	0.00000000	3.01843800	0.00024100
I	2.18998800	-2.16506400	-0.00022500	I	-3.01843400	0.00000000	-0.00024100
I	-2.18712800	-2.16790300	0.00029100	I	0.00000000	-3.01843800	0.00024100
C₈I₆				C₈I₆²⁺			
0 1				2 1			
C	1.16037700	1.28037500	-0.00011500	C	1.19284900	1.31849200	0.00000800
C	-0.03117700	2.17777900	0.00001400	C	0.00034400	2.14683000	0.00003000
C	-1.15258800	1.40660000	0.00004000	C	-1.19220500	1.31875000	-0.00000600
C	-0.72500500	0.00846100	-0.00004600	C	-0.75049100	0.00011600	-0.00001300
C	0.72500500	-0.00846100	-0.00004600	C	0.75049100	-0.00011600	-0.00001300
C	-1.16037700	-1.28037500	-0.00011500	C	-1.19284900	-1.31849200	0.00000800
C	0.03117700	-2.17777900	0.00001400	C	-0.00034400	-2.14683000	0.00003000
C	1.15258800	-1.40660000	0.00004000	C	1.19220500	-1.31875000	-0.00000600
I	-0.05587700	-4.25144900	0.00036300	I	0.00034400	-4.16673400	0.00003400
I	-3.11408500	-1.96547000	-0.00075100	I	-3.11645600	-2.01021400	-0.00004600
I	3.11408500	-2.07300100	0.00040000	I	3.11579900	-2.01075400	0.00000900
I	3.11408500	1.96547000	-0.00075100	I	3.11645600	2.01021400	-0.00004600
I	0.05587700	4.25144900	0.00036300	I	-0.00034400	4.16673400	0.00003400
I	-3.11408500	2.07300100	0.00040000	I	-3.11579900	2.01075400	0.00000900
C₁₀I₈				C₁₀I₈²⁺			
0 1				2 1			
C	2.42639100	0.66015300	0.27846500	C	2.44762000	0.69412100	0.11364000
C	1.23572200	1.34521600	0.36462400	C	1.26328800	1.39228900	0.14059300
C	0.00000000	0.70855800	-0.00012200	C	0.00000200	0.73090600	-0.00012800
C	0.00000000	-0.70850900	0.00012300	C	0.00000100	-0.73090700	0.00013000

C	1.23573800	-1.34517500	-0.36454400
C	2.42640600	-0.66011800	-0.27832700
C	-1.23572200	1.34508900	-0.36509000
C	-1.23573900	-1.34504800	0.36501100
C	-2.42640500	-0.66002000	0.27855800
C	-2.42639000	0.66005700	-0.27869600
I	1.09656900	-3.15962100	-1.44953900
I	-1.09656800	-3.15911800	1.45063500
I	-4.23125300	-1.50252800	0.98306300
I	-4.23118900	1.50253600	-0.98335900
I	-1.09651200	3.15910000	-1.45081000
I	1.09651500	3.15960100	1.44971500
I	4.23118800	1.50288500	0.98283300
I	4.23125000	-1.50287900	-0.98253800

C₁₄I₁₀

0 1

C	3.61151500	-0.49811100	0.52411200
C	2.43405200	-1.11735800	0.83856300
C	1.19384900	-0.68608700	0.21664900
C	1.19395600	0.68563700	-0.21694800
C	2.43425800	1.11670200	-0.83878600
C	3.61169100	0.49810800	-0.52328200
C	-0.00065900	-1.39503100	0.00008300
C	-0.00007500	1.39529200	-0.00002800
C	-1.19413500	0.68644200	0.21668000
C	-1.19427900	-0.68558200	-0.21666700
C	-2.43464900	-1.11602900	-0.83938800
C	-3.61185400	-0.49726100	-0.52405800
C	-3.61176600	0.49789300	0.52458300
C	-2.43448300	1.11703300	0.83934100
I	2.27523000	2.31275100	-2.58218500
I	0.00196600	3.50590000	0.00177000
I	-2.27553500	2.31385300	2.58214500
I	-5.40074100	0.88003100	1.57856200
I	-5.40102400	-0.88005600	-1.57756500
I	-2.27502200	-2.31092200	-2.58348100
I	-0.00156300	-3.50580800	-0.00102900
I	2.27497000	-2.31650400	2.57969900
I	5.40062200	-0.88318700	1.57687400
I	5.40138900	0.88375700	-1.57488700

C₁₆I₁₀

0 1

C	3.27466000	-0.00029500	-0.75828700
C	2.65173600	-1.21997300	-0.43985400
C	1.39888500	-1.23198700	0.19312000
C	0.71994500	-0.00002700	0.33913700
C	1.39901100	1.23186400	0.19291600
C	2.65187900	1.21955500	-0.44001100
C	0.67722100	-2.37075100	0.76670500
C	-0.71996500	0.00003400	0.33913300
C	-1.39900600	-1.23188600	0.19302200
C	-0.67745500	-2.37072000	0.76658800
C	-2.65183500	-1.21968200	-0.43998300
C	-3.27463600	0.00009300	-0.75833600
C	-2.65180500	1.21983000	-0.43991500
C	-1.39894300	1.23196800	0.19302500
C	-0.67726000	2.37081600	0.76651500
C	0.67743800	2.37078900	0.76637700
I	-5.17599800	0.00013600	-1.68154000
I	-3.39247000	-3.04314100	-1.21906800
I	-1.79735200	-3.65825300	2.02434000
I	1.79682600	-3.65810200	2.02490800
I	3.39200800	-3.04367300	-1.21869200
I	5.17621600	-0.00038300	-1.68135200

C	1.26329700	-1.39229200	-0.14050000
C	2.44762900	-0.69412500	-0.11345300
C	-1.26328800	1.39223400	-0.14107000
C	-1.26330000	-1.39223500	0.14098000
C	-2.44763100	-0.69408900	0.11369000
C	-2.44762200	0.69408800	-0.11387400
I	1.51950000	-3.45246600	-0.56195600
I	-1.51956200	-3.45224600	0.56314100
I	-4.29296500	-1.64113500	0.43202700
I	-4.29292900	1.64113600	-0.43235500
I	-1.51952400	3.45224900	-0.56322900
I	1.51946800	3.45246700	0.56204400
I	4.29298900	1.64117400	0.43174000
I	4.29302200	-1.64117700	-0.43141300

C₁₄I₁₀²⁺

2 1

C	3.64656700	-0.58161100	0.41522800
C	2.47118700	-1.23450900	0.65804200
C	1.21640800	-0.70274500	0.17606100
C	1.21638700	0.70277600	-0.17583900
C	2.47110300	1.23457900	-0.65788300
C	3.64651100	0.58160100	-0.41538000
C	0.00006700	-1.38688100	0.00012100
C	0.00000200	1.38684800	0.00008000
C	-1.21635300	0.70274300	0.17591600
C	-1.21630800	-0.70282300	-0.17584800
C	-2.47103400	-1.23471200	-0.65778500
C	-3.64646800	-0.58180300	-0.41523400
C	-3.64652200	0.58159000	0.41510200
C	-2.47115300	1.23457900	0.65770100
I	2.54778700	2.82832900	-2.04599000
I	0.00004200	3.50111100	0.00047200
I	-2.54820500	2.82858200	2.04549100
I	-5.46079000	1.20158900	1.26608300
I	-5.46068100	-1.20185800	-1.26631100
I	-2.54778500	-2.82858800	-2.04574300
I	0.00010800	-3.50114500	-0.00001000
I	2.54795600	-2.82792100	2.04651100
I	5.46087900	-1.20130200	1.26636800
I	5.46064500	1.20124300	-1.26690600

C₁₆I₁₀²⁺

2 1

C	3.35043200	-0.00032000	0.64683000
C	2.73825700	1.21361600	0.32865900
C	1.42213200	1.23854400	-0.16297400
C	0.71718500	-0.00008400	-0.23824200
C	1.42181900	-1.23887100	-0.16269400
C	2.73787900	-1.21418600	0.32916100
C	0.67912900	2.40070900	-0.61763700
C	-0.71712400	0.00004800	-0.23822000
C	-1.42175700	1.23883100	-0.16266300
C	-0.67859400	2.40086900	-0.61736200
C	-2.73781300	1.21415400	0.32917900
C	-3.35038400	0.00030200	0.64685400
C	-2.73821500	-1.21362300	0.32866900
C	-1.42207800	-1.23857600	-0.16293600
C	-0.67908500	-2.40074000	-0.61758000
C	0.67864800	-2.40089400	-0.61740800
I	-5.18548400	0.00039600	1.67766800
I	-3.80936500	2.96341700	0.81906800
I	-1.68578600	3.96246100	-1.62861800
I	1.68614600	3.96194900	-1.62961100
I	3.81075500	2.96262100	0.81743000
I	5.18555100	-0.00034700	1.67761900

I	3.39265600	3.04295700	-1.21899400
I	1.79719400	3.65859900	2.02393300
I	-1.79678200	3.65835900	2.02458500
I	-3.39228400	3.04354300	-1.21851500

I	3.80950000	-2.96338600	0.81918600
I	1.68571200	-3.96243500	-1.62889000
I	-1.68625800	-3.96204400	-1.62929900
I	-3.81082000	-2.96260800	0.81733700