Supplementary Information

Oxidation-induced σ-aromaticity in halogenated cycloalkanes

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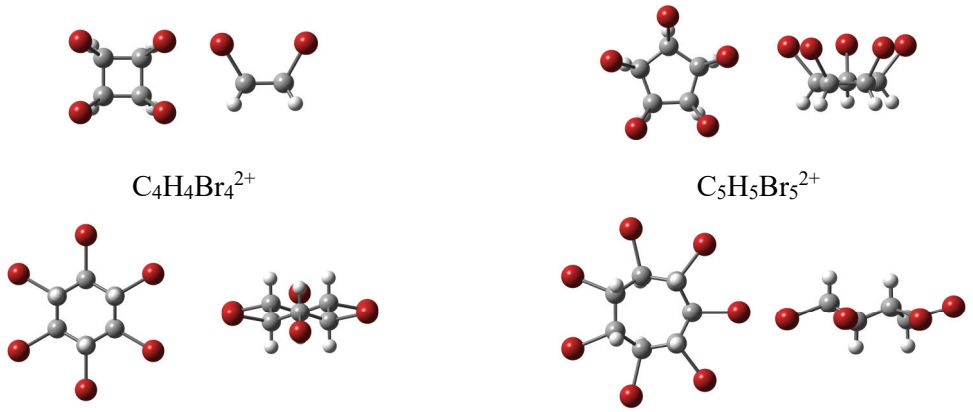


Figure S1 Top and side views of the optimized structures for the studied dicationic bromo-cycloalkanes.

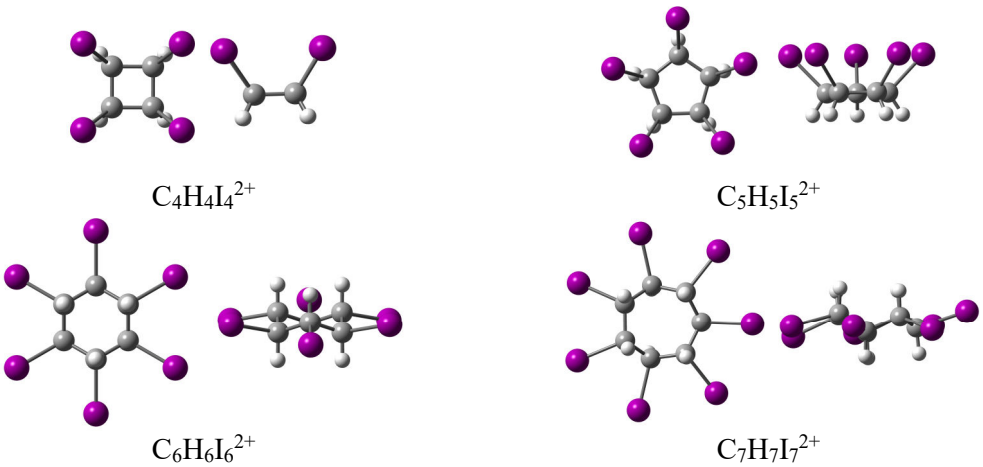
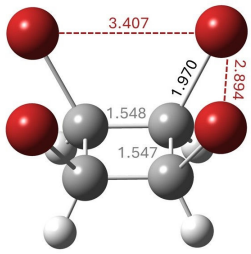
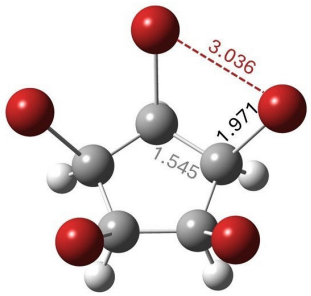


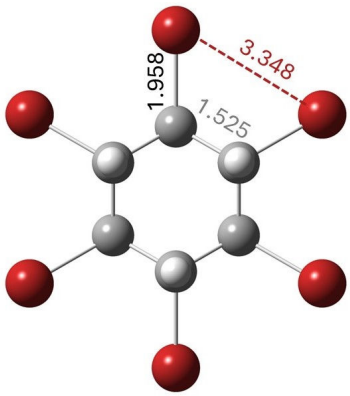
Figure S2 Top and side views of the optimized structures for the studied dicationic iodo-cycloalkanes.



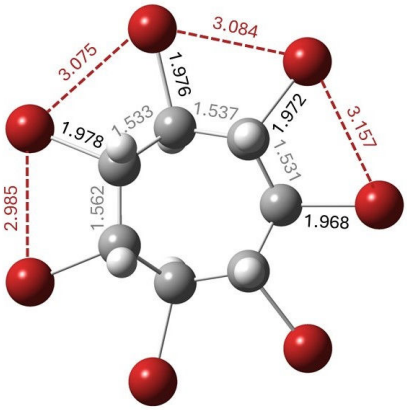
$C_4H_4Br_4^{2+}$



$C_5H_5Br_5^{2+}$



$C_6H_6Br_6^{2+}$



$C_7H_7Br_7^{2+}$

Figure S3 Optimized geometries of the dicationic bromo-cycloalkanes, showing key interatomic distances (in Å).

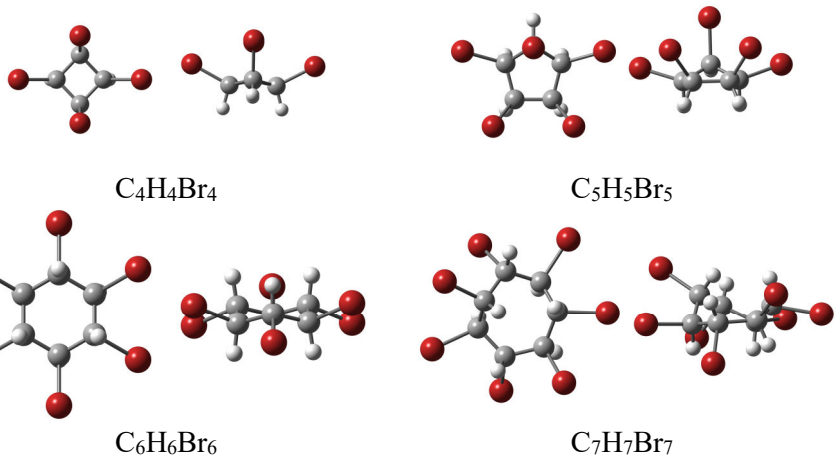


Figure S4 Top and side views of the optimized structures for neutral bromo-cycloalkanes.

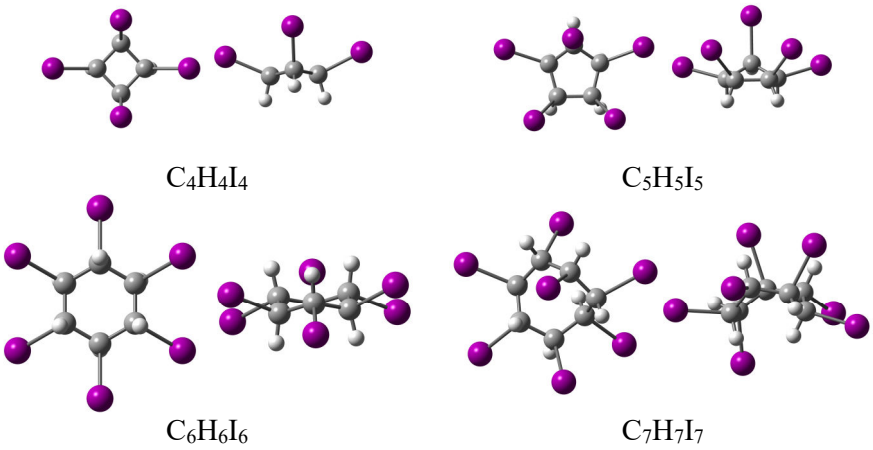


Figure S5 Top and side views of the optimized structures for neutral iodo-cycloalkanes.

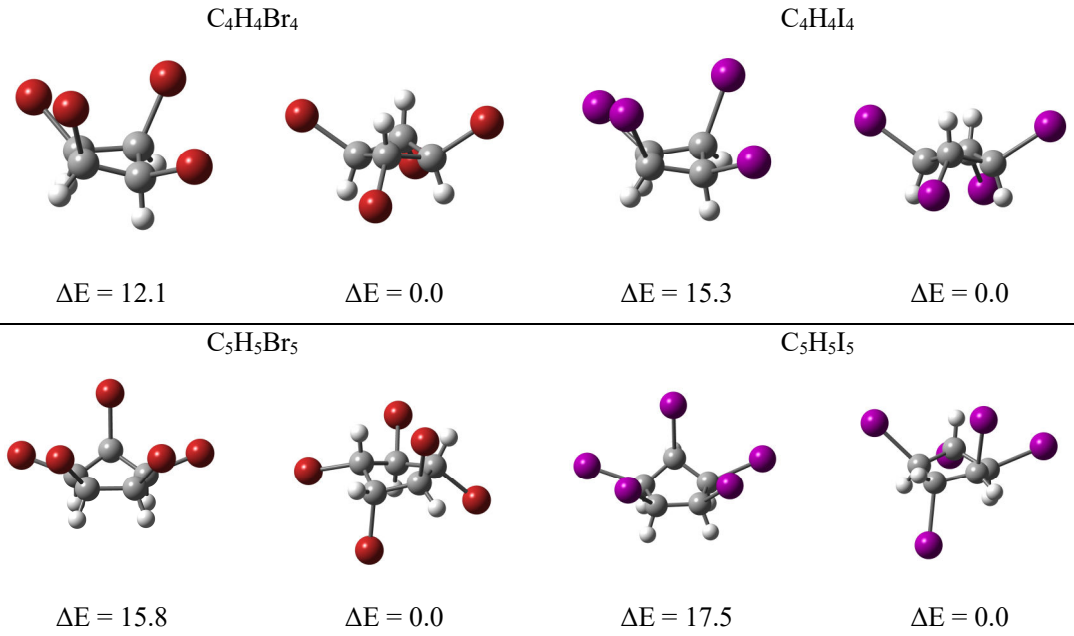
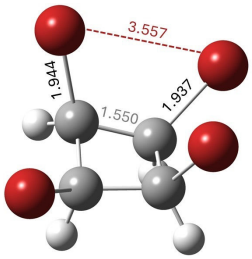
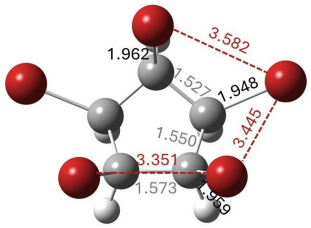


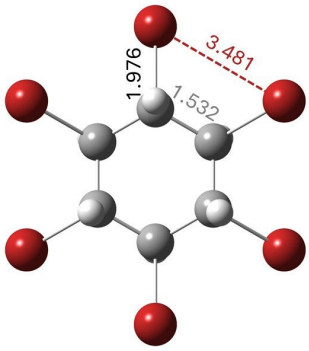
Figure S6 Optimized geometries and relative energies (in kcal mol^{-1}) of the conformers presented in Figures S4 and S5, along with more stable conformers found for the four- and five-membered ring systems.



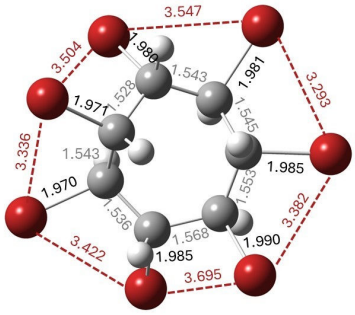
$C_4H_4Br_4$



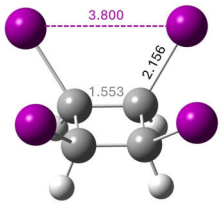
$C_5H_5Br_5$



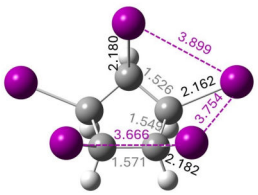
$C_6H_6Br_6$



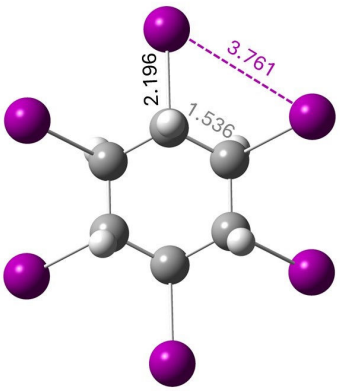
$C_7H_7Br_7$



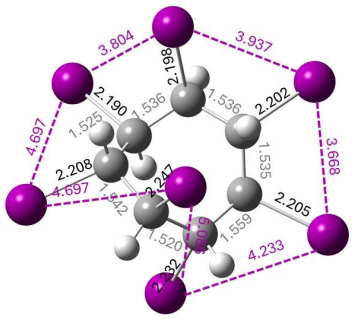
$C_4H_4I_4$



$C_5H_5I_5$



$C_6H_6I_6$



$C_7H_7I_7$

Figure S7 Optimized geometries of neutral bromo- and iodo-cycloalkanes, showing key interatomic distances (in Å).

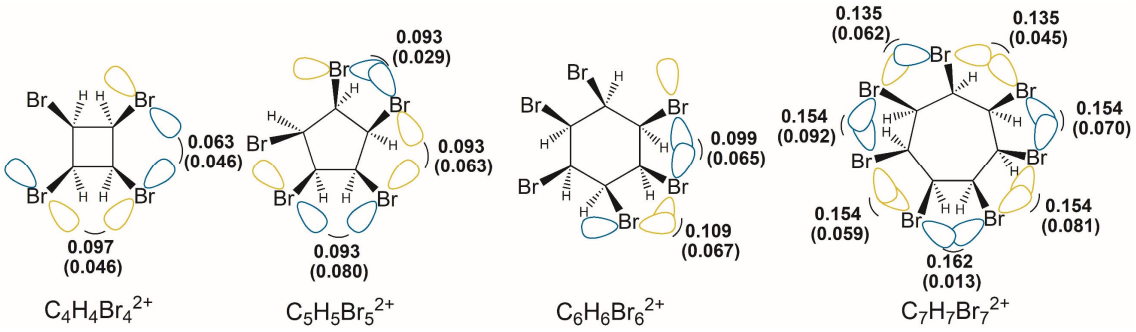


Figure S8 Absolute values of the overlap integrals between in-plane lone pair PNBOs on bromine atoms in dicationic bromo-cycloalkanes. Values in parentheses correspond to the neutral species.

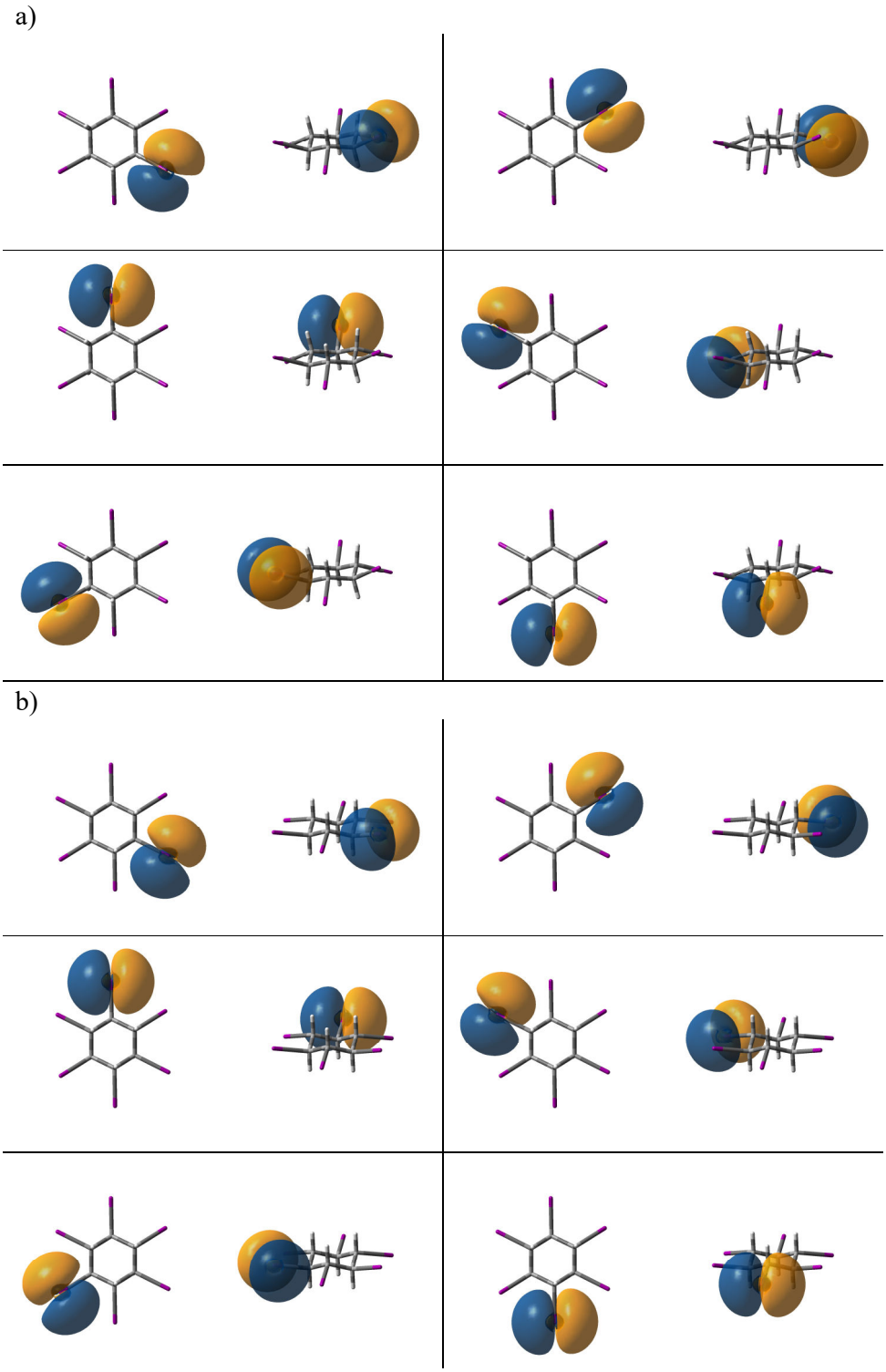
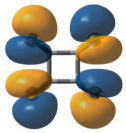
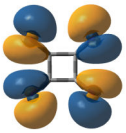
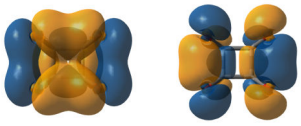
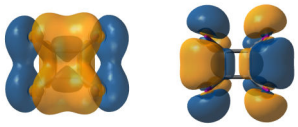
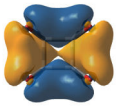
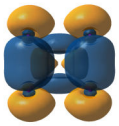
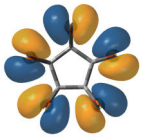
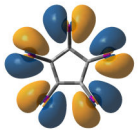
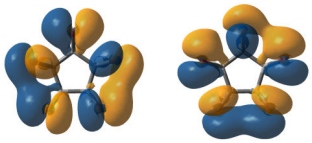
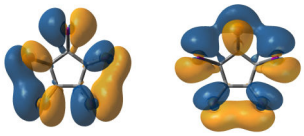
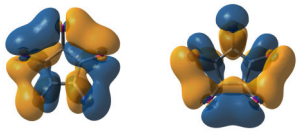
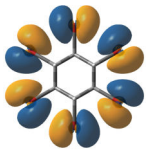
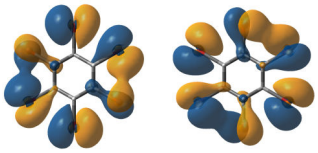


Figure S9 Top and side views of in-plane lone pair PNBOs (isovalue is 0.02e) on the iodine atoms in $C_6H_6I_6$ (a) and $C_6H_6I_6^{2+}$ (b) obtained from NBO analysis at the B3LYP/def2-TZVP level of theory.

$C_4H_4Br_4^{2+}$	$C_4H_4I_4^{2+}$
 LUMO	 LUMO
 HOMO-3	 HOMO-4
 HOMO-8	 HOMO-6
$C_5H_5Br_5^{2+}$	$C_5H_5I_5^{2+}$
 LUMO	 LUMO
 HOMO-1	 HOMO-1
 HOMO-4	 HOMO-5
$C_6H_6Br_6^{2+}$	
 LUMO	
 HOMO	

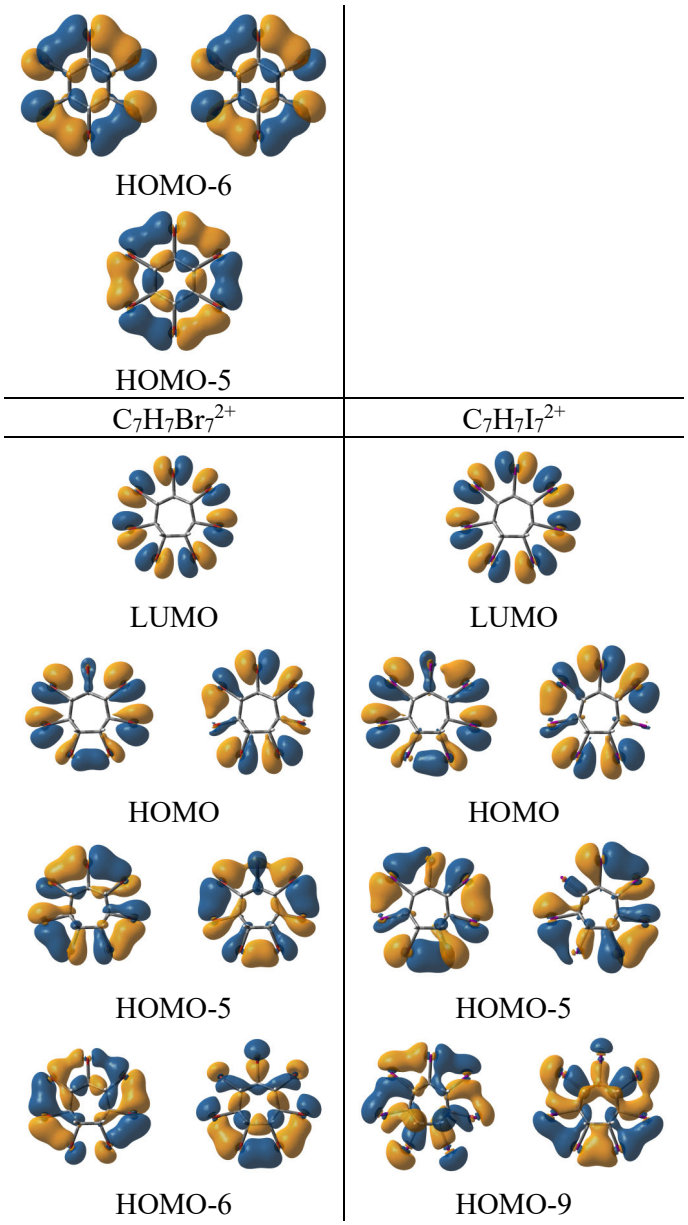
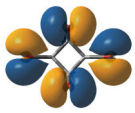
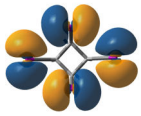
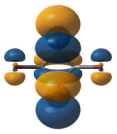
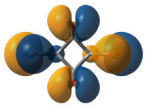
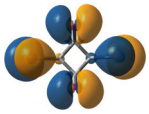
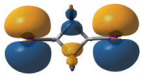
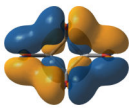
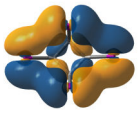
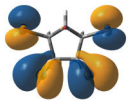
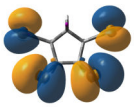
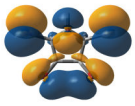
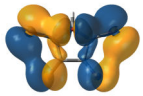
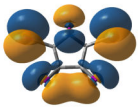
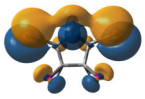
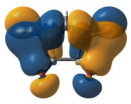
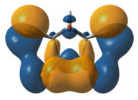
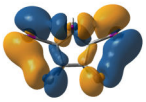
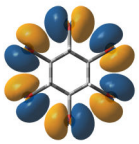
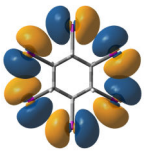
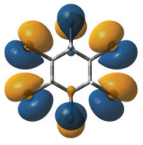
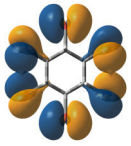
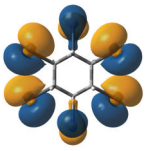
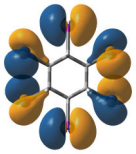


Figure S10 Canonical σ-type molecular orbitals of $C_4H_4Br_4^{2+}$, $C_4H_4I_4^{2+}$, $C_5H_5Br_5^{2+}$, $C_5H_5I_5^{2+}$, $C_6H_6Br_6^{2+}$, $C_7H_7Br_7^{2+}$ and $C_7H_7I_7^{2+}$.

$C_4H_4Br_4$	$C_4H_4I_4$
 HOMO-2	 HOMO
 HOMO  HOMO-1	 HOMO-2  HOMO-4
 HOMO-4	 HOMO-5
$C_5H_5Br_5$	$C_5H_5I_5$
 HOMO	 HOMO
 HOMO-3  HOMO-4	 HOMO-3  HOMO-4
 HOMO-5  HOMO-6	 HOMO-5  HOMO-7
$C_6H_6Br_6$	$C_6H_6I_6$
 HOMO	 HOMO
  HOMO-1	  HOMO-1

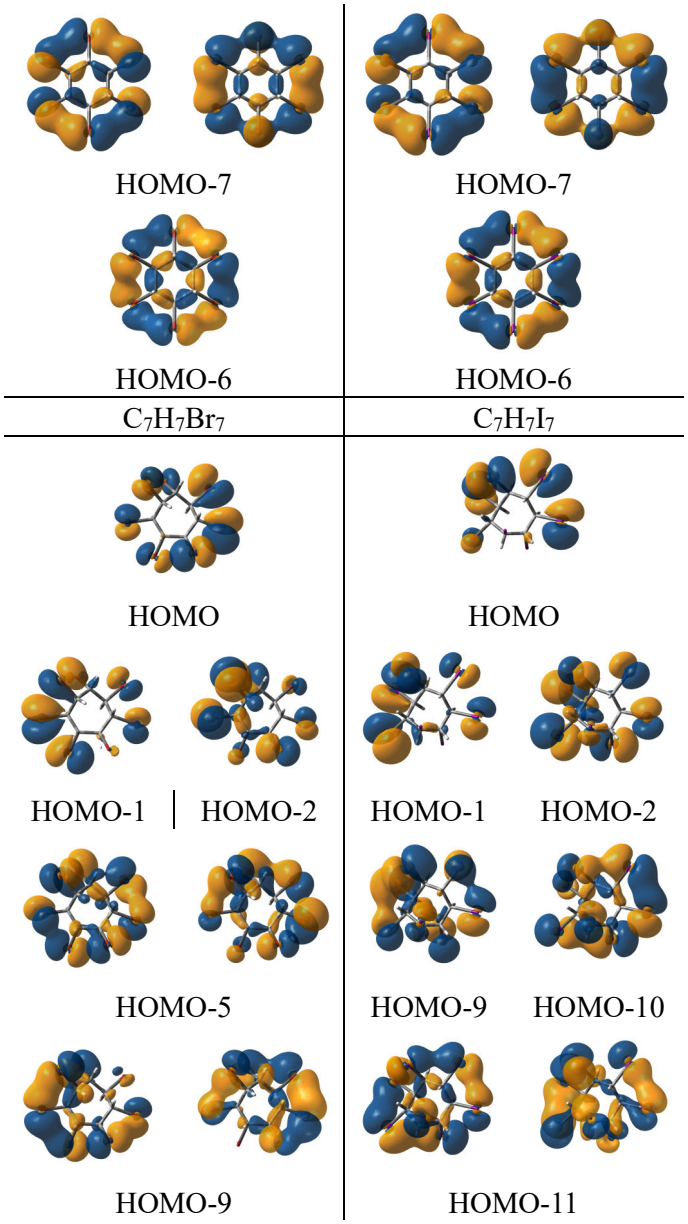


Figure S11 Canonical σ-type molecular orbitals of $C_4H_4Br_4$, $C_4H_4I_4$, $C_5H_5Br_5$, $C_5H_5I_5$, $C_6H_6Br_6$, $C_7H_7Br_7$ and $C_7H_7I_7$.

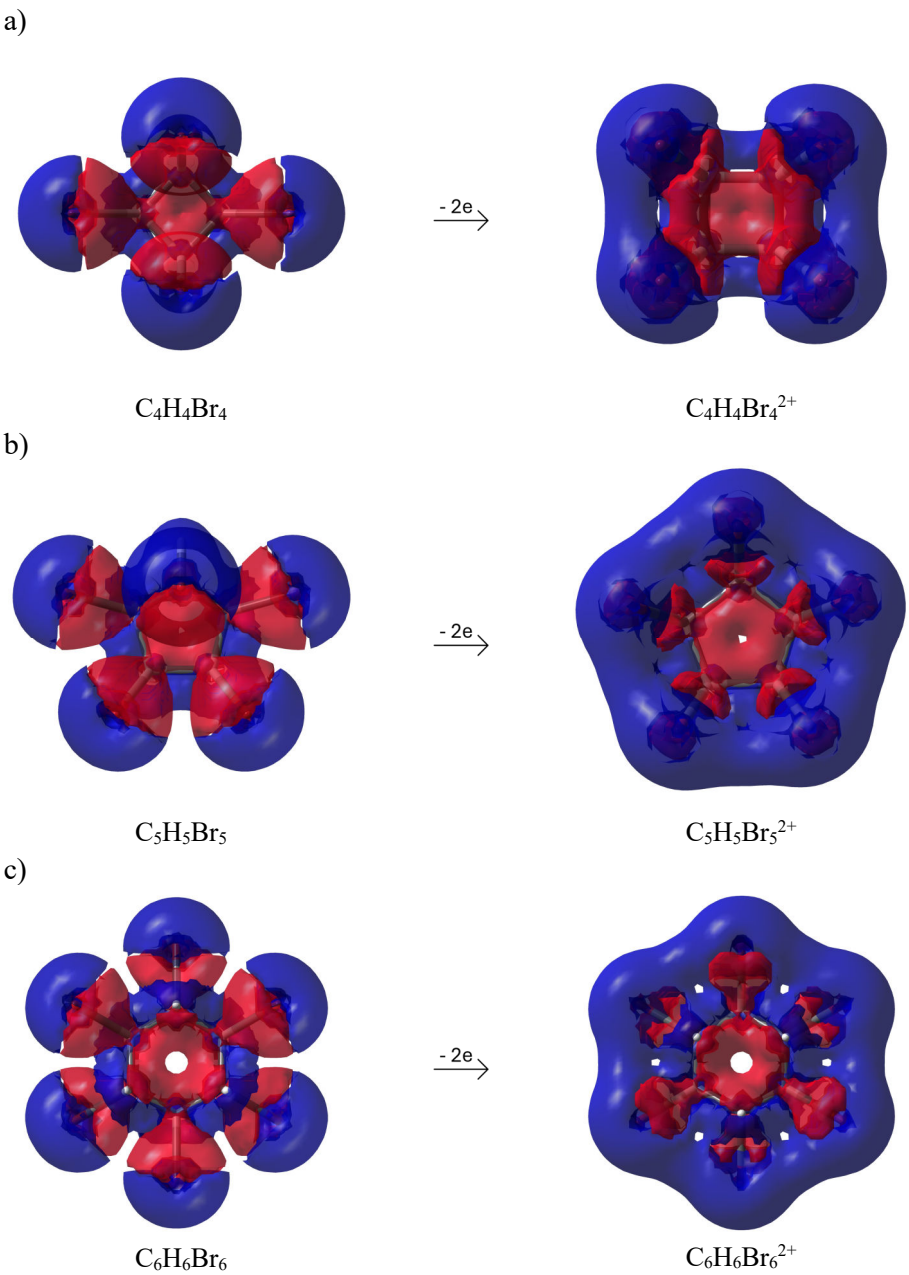
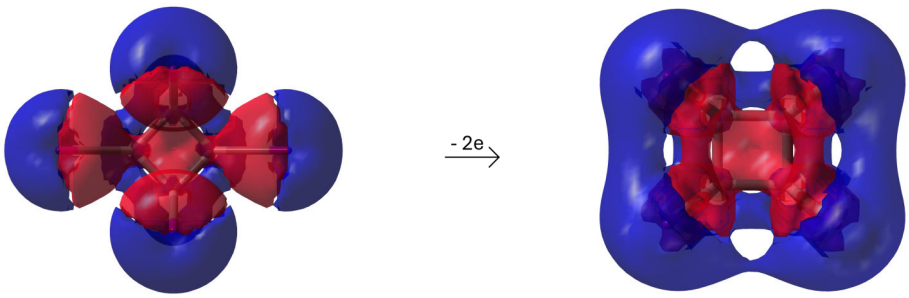


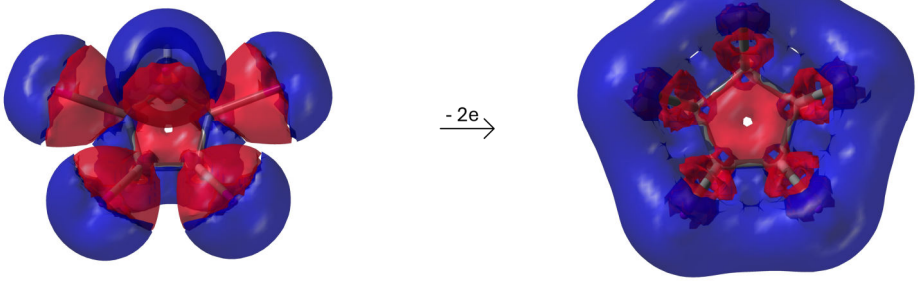
Figure S12 Signed modulus of the magnetically induced current density in the neutral and dicationic (oxidized) forms of: $C_4H_4Br_4$ (a), $C_5H_5Br_5$ (b), $C_6H_6Br_6$ (c), $C_4H_4I_4$ (d), $C_5H_5I_5$ (e) and $C_7H_7I_7$ (f). The diatropic current density is shown in blue and the paratropic one in red. The isosurface value is set to ±0.02 a.u.

d)



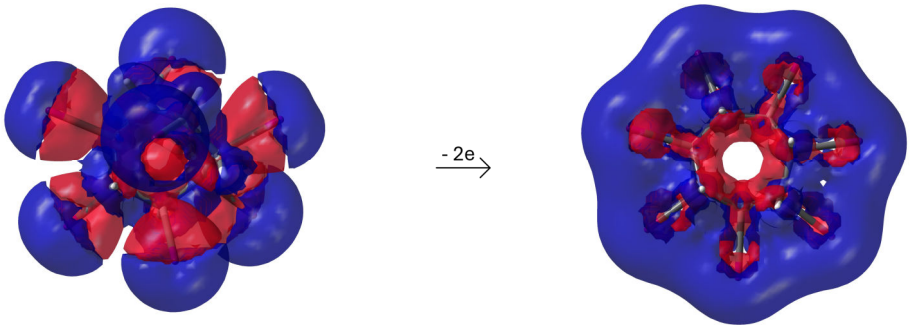
$C_4H_4I_4$ $C_4H_4I_4^{2+}$

e)



$C_5H_5I_5$ $C_5H_5I_5^{2+}$

f)



$C_7H_7I_7$ $C_7H_7I_7^{2+}$

Figure S12 Continuation.

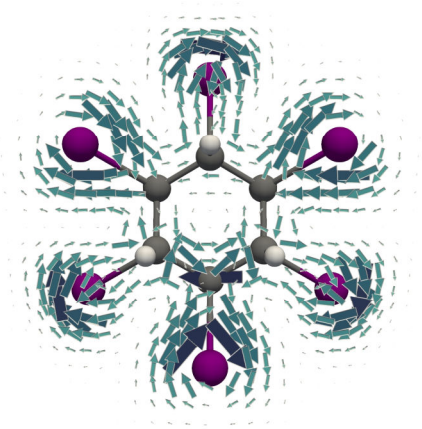


Figure S13 Total current density maps plotted 1 Bohr above the surface which adopts the molecular shape for $C_6H_6I_6$.

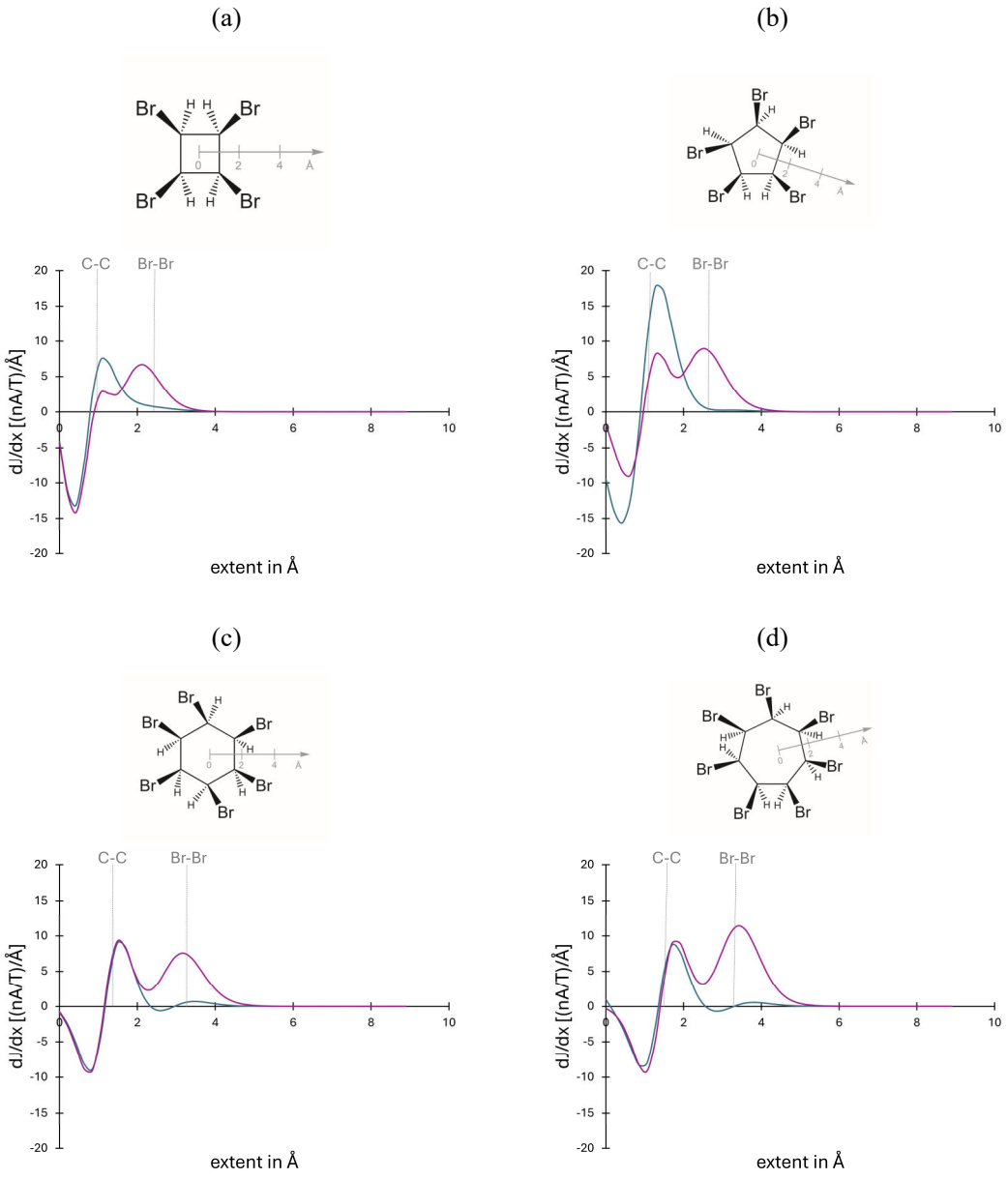


Figure S14 Profiles of bond current strengths of neutral (blue line) and dicationic (purple line) bromo-substituted cycloalkanes: (a) $C_4H_4Br_4$; (b) $C_5H_5Br_5$; (c) $C_6H_6Br_6$; (d) $C_7H_7Br_7$. Positive and negative current strengths indicate diatropic and paratropic ring currents, respectively.

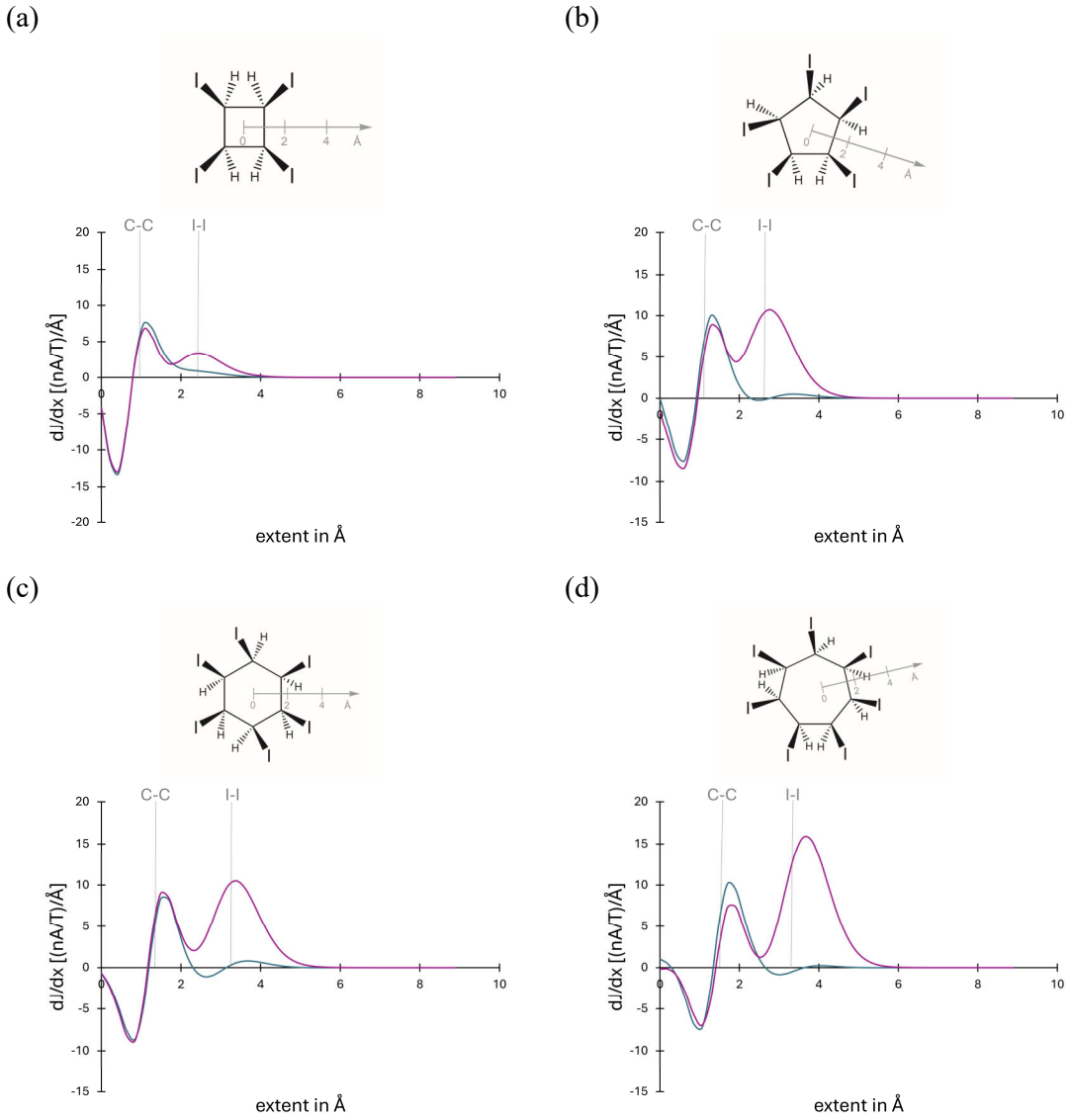


Figure S15 Profiles of bond current strengths of neutral (blue line) and dicationic (purple line) iodo-substituted cycloalkanes: $C_4H_4I_4$ (a); $C_5H_5I_5$ (b); $C_6H_6I_6$ (c) and $C_7H_7I_7$ (d). Positive and negative current strengths indicate diatropic and paratropic ring currents, respectively.

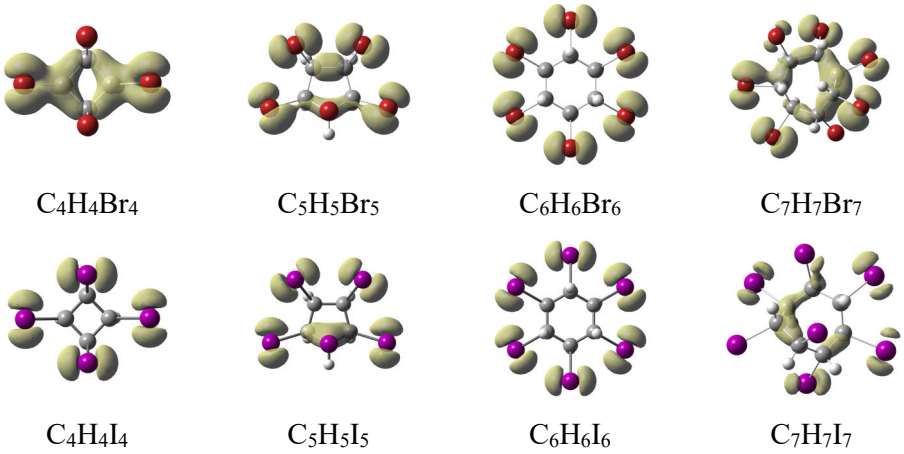


Figure S16 Top view of the $EDDB_H$ function isosurfaces (isovalue 0.001 a.u.) for neutral halogenated cycloalkanes.

Table S1 Calculated bond current strengths (I, in nA T^{-1}) and EDDB (in a.u.) values the carbon atom rings in the studied halogenated cycloalkanes in their neutral and dicationic forms.

	I		EDDB	
	neutral	oxidized	neutral	oxidized
$C_4H_4Br_4$	-2.2	-4.8	0.231	0.213
$C_5H_5Br_5$	2.3	0.2	0.321	0.353
$C_6H_6Br_6$	-0.8	-0.8	0.494	0.492
$C_7H_7Br_7$	-1.4	-2.2	0.536	0.523
$C_4H_4I_4$	-2.3	-4.9	0.311	0.294
$C_5H_5I_5$	2.5	1.0	0.417	0.448
$C_6H_6I_6$	-0.9	-0.5	0.599	0.577
$C_7H_7I_7$	-1.5	-0.7	0.671	0.655

Table S2 Cartesian coordinates of the optimized geometries for the studied molecules obtained at the B3LYP/def2-TZVP level of theory.

$C_4H_4Br_4$				$C_4H_4Br_4^{2+}$			
0 1				2 1			
C	-1.05688400	-0.00028200	-1.20986200	C	-0.77377100	0.77352100	-1.31359400
C	0.00001000	-1.10643700	-0.96369400	C	-0.77425700	-0.77326700	-1.31354700
C	1.05675200	-0.00012800	-1.20997700	C	0.77338200	-0.77374000	-1.31369200
C	-0.00011500	1.10611000	-0.96406500	C	0.77386800	0.77304800	-1.31390400
H	-1.32097300	-0.00052400	-2.26591700	H	-1.23861100	1.26988100	-2.16238400
H	0.00000800	-1.92462100	-1.67547600	H	-1.23933100	-1.26940900	-2.16233700
H	1.32072600	-0.00024000	-2.26606100	H	1.23796700	-1.27023600	-2.16254200
H	-0.00019100	1.92405200	-1.67612400	H	1.23868700	1.26904200	-2.16292000
Br	2.76648900	-0.00009700	-0.29893000	Br	1.70305700	-1.44741400	0.28697200
Br	0.00010600	1.95655800	0.78372300	Br	1.70412100	1.44656000	0.28649800
Br	-2.76652100	-0.00000600	-0.29862900	Br	-1.70297300	1.44744800	0.28724100
Br	-0.00002100	-1.95629000	0.78438300	Br	-1.70403500	-1.44649900	0.28725000
$C_5H_5Br_5$				$C_5H_5Br_5^{2+}$			
0 1				2 1			
C	1.16126600	0.67488200	-1.06917200	C	-0.85739000	0.99589500	-1.23495700
C	-0.00006600	1.40845800	-0.40260900	C	-1.21204200	-0.50750800	-1.23557100
C	-1.16132900	0.67478300	-1.06917300	C	0.10826600	-1.30945100	-1.23499700
C	-0.78662800	-0.82918400	-1.10805500	C	1.27883700	-0.30160300	-1.23555600
C	0.78666200	-0.82912700	-1.10808900	C	0.68205900	1.12317300	-1.23507600
H	1.16834100	1.01236200	-2.10677300	H	-1.27922200	1.48594400	-2.10803100
H	-0.00011000	2.46904800	-0.62913200	H	-1.80747700	-0.75674900	-2.10950800
H	-1.16839600	1.01223300	-2.10678900	H	0.16170900	-1.95445000	-2.10760600
H	-1.13729800	-1.26289700	-2.03830800	H	1.90726700	-0.44993400	-2.10933400
H	1.13730200	-1.26274500	-2.03840300	H	1.01743600	1.67575500	-2.10830000
Br	-2.94815800	1.17139000	-0.47254500	Br	0.21326300	-2.57325500	0.27357300
Br	-1.67562700	-1.95186300	0.22900600	Br	2.51528200	-0.59388200	0.27083300
Br	1.67583600	-1.95181900	0.22888300	Br	1.34079600	2.20816000	0.27240400
Br	2.94805200	1.17158200	-0.47246800	Br	-1.68519800	1.95739100	0.27279300
Br	-0.00008100	1.31594200	1.55746600	Br	-2.38408800	-0.99851700	0.27039000
$C_6H_6Br_6$				$C_6H_6Br_6^{2+}$			
0 1				2 1			
C	0.00000000	1.47147300	0.21356600	C	-1.23310000	0.71193000	0.27251200
C	1.27433300	0.73573700	-0.21356600	C	0.00000000	1.42386100	-0.27251200
C	1.27433300	-0.73573700	0.21356600	C	1.23310000	0.71193000	0.27251200
C	0.00000000	-1.47147300	-0.21356600	C	1.23310000	-0.71193000	-0.27251200
C	-1.27433300	-0.73573700	0.21356600	C	0.00000000	-1.42386100	0.27251200
C	-1.27433300	0.73573700	-0.21356600	C	-1.23310000	-0.71193000	-0.27251200
H	1.41847200	0.81895500	-1.28823400	H	0.00000000	1.43859100	-1.36150400
H	0.00000000	1.63791100	1.28823400	H	-1.24585600	0.71929600	1.36150400
H	0.00000000	-1.63791100	-1.28823400	H	1.24585600	-0.71929600	-1.36150400
H	-1.41847200	-0.81895500	1.28823400	H	0.00000000	-1.43859100	1.36150400
H	-1.41847200	0.81895500	-1.28823400	H	-1.24585600	-0.71929600	-1.36150400
H	1.41847200	-0.81895500	1.28823400	H	1.24585600	0.71929600	1.36150400
Br	2.83936000	1.63930500	0.58546200	Br	0.00000000	3.31489400	0.23364100
Br	0.00000000	3.27861100	-0.58546200	Br	-2.87078200	1.65744700	-0.23364100
Br	2.83936000	-1.63930500	-0.58546200	Br	2.87078200	1.65744700	-0.23364100
Br	0.00000000	-3.27861100	0.58546200	Br	2.87078200	-1.65744700	0.23364100
Br	-2.83936000	-1.63930500	-0.58546200	Br	0.00000000	-3.31489400	-0.23364100
Br	-2.83936000	1.63930500	0.58546200	Br	-2.87078200	-1.65744700	0.23364100
$C_7H_7Br_7$				$C_7H_7Br_7^{2+}$			
0 1				2 1			
C	-1.42543800	-0.54108500	-0.26015200	C	-0.37170200	-1.51114500	-0.19604700
C	-0.37306700	-1.64556000	-0.08496200	C	1.05035500	-1.28274600	0.33967400
C	1.14942400	-1.28040700	-0.00106000	C	1.68555200	0.00235900	-0.19789200
C	-1.17682100	0.54539700	0.80731400	C	-1.45645300	-0.78299100	0.60615900
C	1.67695300	0.11261200	0.43941700	C	1.04672200	1.28589300	0.33914200
C	-0.34286000	1.69587100	0.24564900	C	-1.45853200	0.77856600	0.60640100
C	1.02076600	1.27404500	-0.34013700	C	-0.37620200	1.51006000	-0.19611600
H	-1.39864400	-0.09706400	-1.25053600	H	-0.43217900	-1.29794300	-1.26197400
H	-0.64437900	-2.20947000	0.80122900	H	1.07039600	-1.31252700	1.42852300

H	1.59631400	-1.48292700	-0.96804200	H	1.68202700	0.00209400	-1.28741500
H	1.59633000	0.26604600	1.51203600	H	1.06699100	1.31627800	1.42797100
H	-0.62509700	0.10420600	1.63567000	H	-1.41414000	-1.11608900	1.64087400
H	-0.18189800	2.42152500	1.03581200	H	-1.41646600	1.11141200	1.64121300
H	0.93158600	1.00074300	-1.38851400	H	-0.43638900	1.29695800	-1.26207900
Br	-0.51870200	-2.97036700	-1.55577500	Br	2.20424700	-2.78786300	-0.20211200
Br	1.93610600	-2.66735800	1.18939300	Br	3.59525700	0.00518300	0.27787300
Br	3.63524200	0.05454800	0.11935500	Br	2.19621900	2.79400900	-0.20374100
Br	2.10817400	2.92927400	-0.37780300	Br	-0.81770600	3.43204500	-0.06963000
Br	-1.34902100	2.69683700	-1.13490400	Br	-3.19932100	1.48798100	-0.01005000
Br	-2.72674800	1.29614600	1.76610300	Br	-3.19486600	-1.49699100	-0.01161200
Br	-3.21213500	-1.36674500	-0.18391400	Br	-0.80779200	-3.43436900	-0.07030100
$C_4H_4I_4$				$C_4H_4I_4^{2+}$			
0 1				2 1			
C	1.05297100	-0.00023900	-1.35144400	C	-0.77339700	-0.77155600	-1.46586600
C	0.00001800	-1.10681100	-1.10528600	C	-0.77021100	0.77485400	-1.46543200
C	-1.05285200	-0.00020400	-1.35153600	C	0.77297300	0.77180400	-1.46594800
C	0.00008000	1.10644700	-1.10564100	C	0.76978700	-0.77461100	-1.46577000
H	1.30720900	-0.00041500	-2.41049900	H	-1.22066000	-1.23482000	-2.34179200
H	0.00004200	-1.91785600	-1.82510200	H	-1.21601900	1.24099600	-2.34053400
H	-1.30699700	-0.00036500	-2.41061300	H	1.21996700	1.23518200	-2.34195200
H	0.00011900	1.91726100	-1.82571600	H	1.21532100	-1.24057700	-2.34110700
I	-3.00115000	0.00001500	-0.43746600	I	1.85427100	1.62466500	0.20917100
I	0.00008300	2.12656300	0.79506100	I	1.84721300	-1.63090700	0.21048700
I	3.00118900	-0.00015400	-0.43720300	I	-1.85421700	-1.62466300	0.20945900
I	-0.00015300	-2.12630600	0.79574700	I	-1.84714500	1.63083500	0.21132600
$C_5H_5I_5$				$C_5H_5I_5^{2+}$			
0 1				2 1			
C	0.78548200	0.78819300	-1.23174900	C	0.79280900	1.04784500	-1.34959400
C	1.15865400	-0.71375200	-1.17224300	C	1.24109500	-0.43019000	-1.35104800
C	-0.00028400	-1.44039400	-0.49613200	C	-0.02569400	-1.31354000	-1.34885000
C	-1.15900900	-0.71346000	-1.17223900	C	-1.25695700	-0.38127600	-1.35106300
C	-0.78558600	0.78839900	-1.23149400	C	-0.75123400	1.07811300	-1.34956700
H	1.13063200	1.20347500	-2.17221700	H	1.16162300	1.53589000	-2.24724600
H	1.15572900	-1.06238000	-2.20693500	H	1.81645300	-0.62996900	-2.25057200
H	-0.00041100	-2.50246700	-0.71344800	H	-0.03763900	-1.92687700	-2.24534300
H	-1.15596900	-1.06193200	-2.20698800	H	-1.83966800	-0.55835000	-2.25060600
H	-1.13093700	1.20399900	-2.17175000	H	-1.10074800	1.58027600	-2.24715300
I	-0.00008500	-1.38403000	1.68307800	I	-0.05571700	-2.84163200	0.20026600
I	-3.15570500	-1.32137700	-0.60684100	I	-2.72575200	-0.82716900	0.19111200
I	-1.83246700	2.10784500	0.15517000	I	-1.62707800	2.33353000	0.19692000
I	1.83329600	2.10779800	0.15409300	I	1.71720700	2.26814300	0.19673000
I	3.15506400	-1.32221000	-0.60635800	I	2.69133600	-0.93299800	0.19123000
$C_6H_6I_6$				$C_6H_6I_6^{2+}$			
0 1				2 1			
C	0.00000000	1.48001696	0.20465359	C	-1.23806238	0.71479565	0.27064064
C	1.28173229	0.74000848	-0.20465359	C	0.00000000	1.42959129	-0.27064064
C	1.28173229	-0.74000848	0.20465359	C	1.23806238	0.71479565	0.27064064
C	-0.00000000	-1.48001696	-0.20465359	C	1.23806238	-0.71479565	-0.27064064
C	-1.28173229	-0.74000848	0.20465359	C	-0.00000000	-1.42959129	0.27064064
C	-1.28173229	0.74000848	-0.20465359	C	-1.23806238	-0.71479565	-0.27064064
H	1.45877286	0.84222290	-1.27245806	H	0.00000000	1.43820944	-1.35947915
H	0.00000000	1.68444580	1.27245806	H	-1.24552591	0.71910472	1.35947915
H	-0.00000000	-1.68444580	-1.27245806	H	1.24552591	-0.71910472	-1.35947915
H	-1.45877286	-0.84222290	1.27245806	H	-0.00000000	-1.43820944	1.35947915
H	-1.45877286	0.84222290	-1.27245806	H	-1.24552591	-0.71910472	-1.35947915
H	1.45877286	-0.84222290	1.27245806	H	1.24552591	0.71910472	1.35947915
I	3.00522951	1.73507007	0.72473263	I	0.00000000	3.53176568	0.23914149
I	0.00000000	3.47014014	-0.72473263	I	-3.05859880	1.76588284	-0.23914149
I	3.00522951	-1.73507007	-0.72473263	I	3.05859880	1.76588284	-0.23914149
I	-0.00000000	-3.47014014	0.72473263	I	3.05859880	-1.76588284	0.23914149
I	-3.00522951	-1.73507007	-0.72473263	I	-0.00000000	-3.53176568	-0.23914149
I	-3.00522951	1.73507007	0.72473263	I	-3.05859880	-1.76588284	0.23914149
$C_7H_7I_7$				$C_7H_7I_7^{2+}$			
0 1				2 1			

C	-0.06061100	-1.43625800	-0.48496700	C	0.78969000	1.36146100	-0.20145200
C	1.16030400	-0.51867400	-0.68341300	C	-0.66377400	1.54006500	0.28686900
C	-1.40089900	-0.75412200	-0.08804600	C	-1.63748800	0.44936400	-0.18898500
C	1.60988000	0.22640500	0.56848100	C	1.59605400	0.34427000	0.62754500
C	-1.51540200	0.70149200	-0.56030700	C	-1.35728300	-0.95369600	0.37237600
C	0.57831600	1.26897800	1.04538500	C	1.20492200	-1.17169100	0.57109500
C	-0.55887700	1.71408300	0.14048300	C	-0.06537500	-1.57452300	-0.19708700
H	-0.19948600	-1.96806800	-1.41864100	H	0.82962600	1.15648000	-1.26974800
H	0.91786700	0.19338900	-1.47046000	H	-0.68795800	1.63633300	1.37170600
H	-1.58385500	-0.82325300	0.97679200	H	-1.67299200	0.41857400	-1.27718200
H	1.83866100	-0.48249700	1.35492700	H	-1.33752600	-0.94795200	1.46134400
H	-1.39728800	0.74278500	-1.63704400	H	1.55133400	0.64557100	1.67212000
H	1.08371100	2.16335600	1.37934800	H	1.11616100	-1.51634800	1.59864300
H	-1.13788700	2.42359900	0.71343400	H	0.02096400	-1.37600500	-1.26381300
I	-3.53825700	1.54272000	-0.31314900	I	-1.45750400	3.47299400	-0.38807100
I	0.23847000	3.11019800	-1.40715900	I	-3.67391600	1.05052100	0.35312700
I	-0.28397000	0.69835800	3.04003700	I	-3.09164400	-2.22706900	-0.06484100
I	3.54861600	1.26717200	0.38429600	I	-0.16889500	-3.76860000	-0.12810100
I	2.72230500	-1.68266500	-1.68487800	I	2.84245900	-2.45956100	-0.14569900
I	0.32855900	-3.08311400	0.91820500	I	3.73772500	0.63807100	0.21157200
I	-2.98549600	-2.03117300	-0.92837300	I	1.83026400	3.29386800	-0.02506600