

# $\sigma$ -aromaticity in dicationic halogenated cycloalkanes

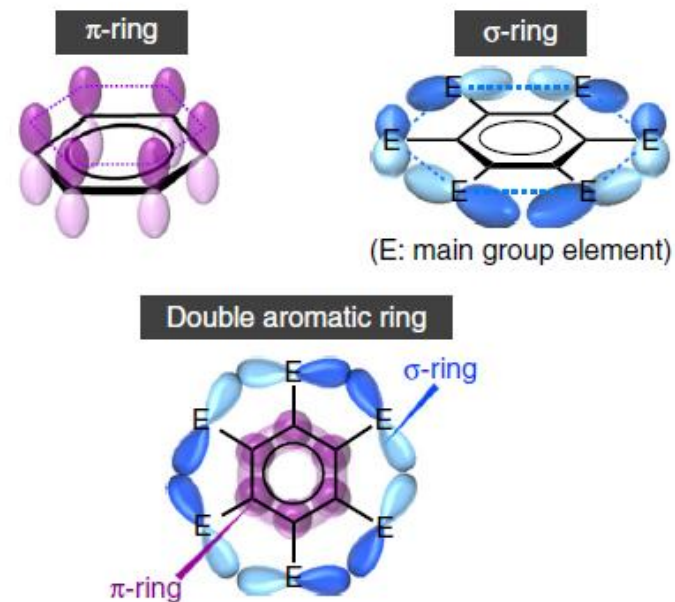
Sladana Đorđević and Slavko Radenković

*Faculty of Science, University of Kragujevac, Kragujevac, Serbia*

✉ [sladjana.djordjevic@pmf.kg.ac.rs](mailto:sladjana.djordjevic@pmf.kg.ac.rs)

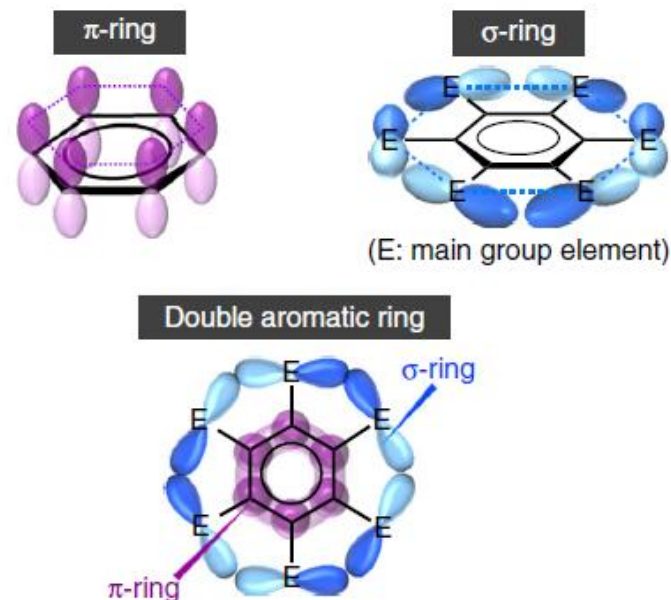
# $\sigma$ -aromaticity

- $\sigma$ -electrons, like  $\pi$ -electrons, can also participate in cyclic delocalization



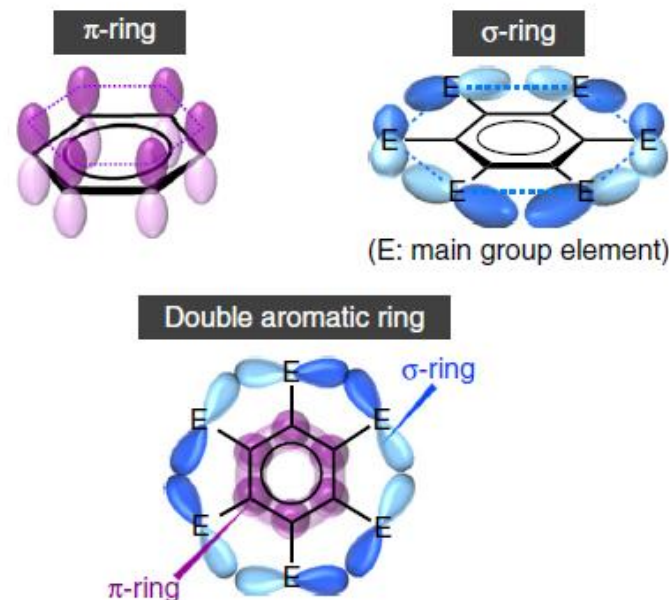
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- 1979 - Schleyer introduced the idea of double aromaticity -  $C_6H_3^+$



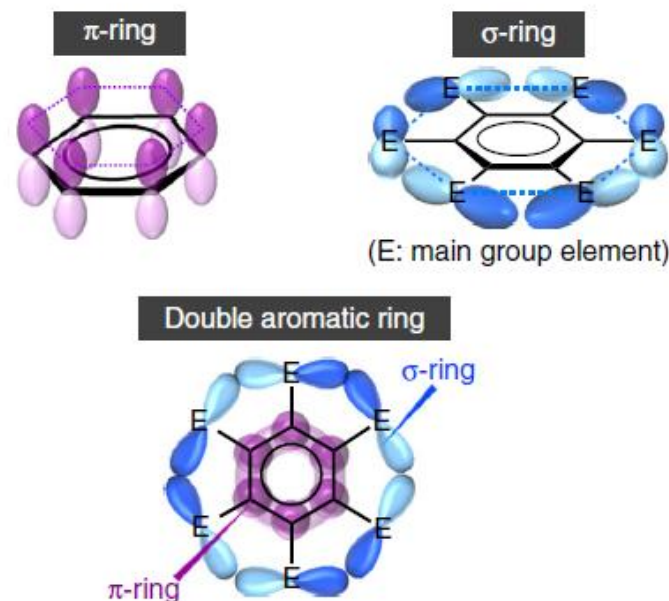
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- 1988 - Experimental validation of double aromaticity followed with the synthesis and characterization of the dication  $C_6I_6^{2+}$
- 2018 - experimentally characterized hexakis(phenylselenenyl)benzene dication



# Aromaticity criteria

## **Electronic nature**

## **Electron delocalization**

**Structure** – tendency toward bond length equalization and planarity

**Energy** – enhanced stability

- resonance energies – RE
- aromatic stabilization energies – ASE
- isomerization stabilization energy – ISE

## **Reactivity**

- lowered reactivity
- electrophilic aromatic substitution (if applicable)

## **Magnetic properties**

- proton chemical shift
- NICS (Nucleus Independent Chemical Shift)
- ring current plots

Chen *et al*, *Chem. Rev.* **2005**, 105, 3842.

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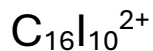
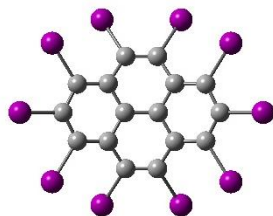
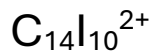
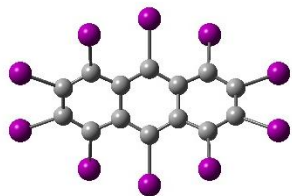
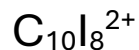
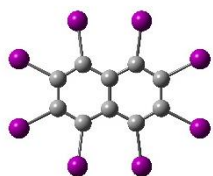
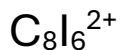
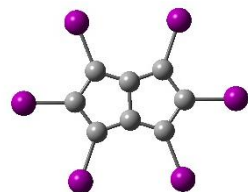
## Magnetic properties

- proton chemical shift
- NICS (Nucleus Independent Chemical Shift)
- **ring current plots**

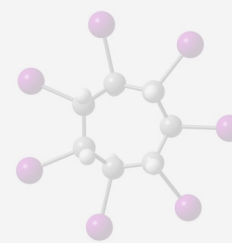
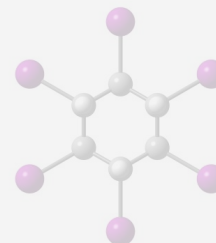
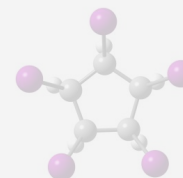
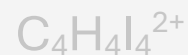
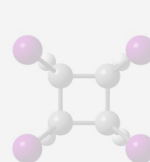
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# $\sigma$ -aromaticity in halogenated hydrocarbons

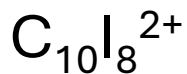
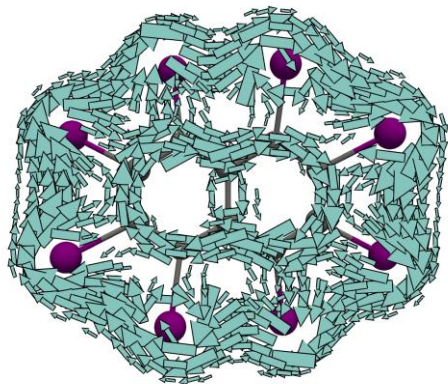
## $\pi$ -aromatic cycles



## nonaromatic cycloalkanes

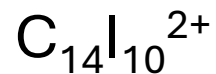
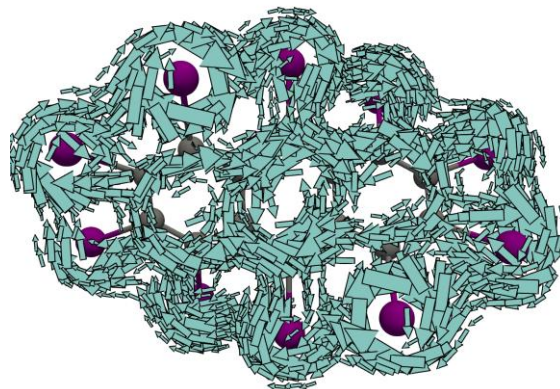


# Periodo-polycyclic hydrocarbons



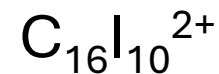
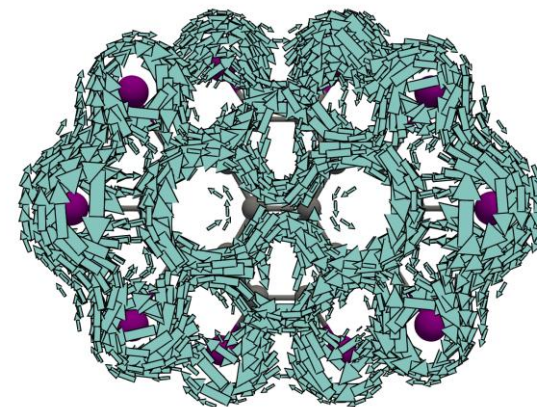
$\pi$ -aromatic

$\sigma$ -aromatic



$\pi$ -aromatic

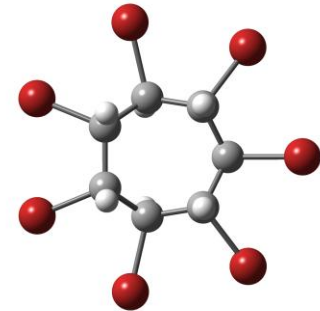
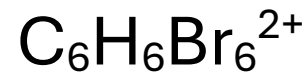
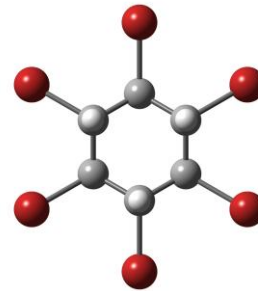
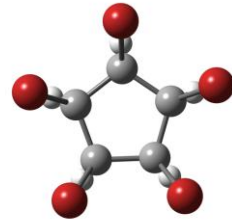
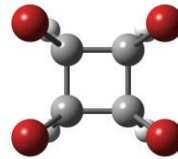
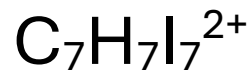
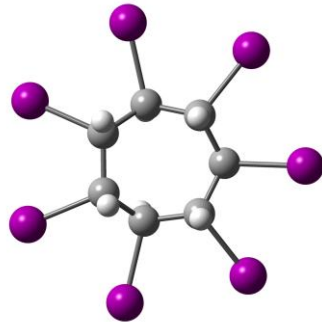
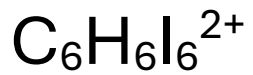
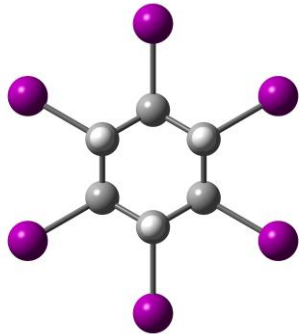
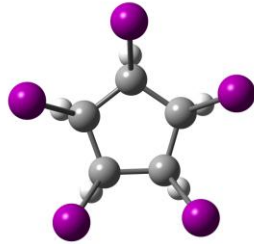
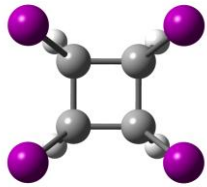
$\sigma$ -aromatic



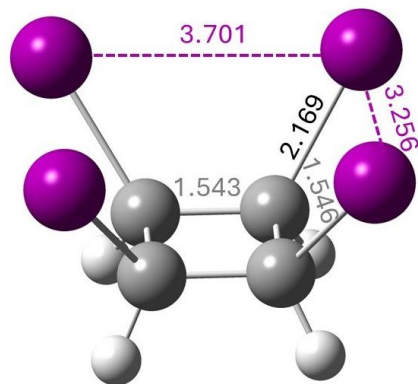
$\pi$ -aromatic

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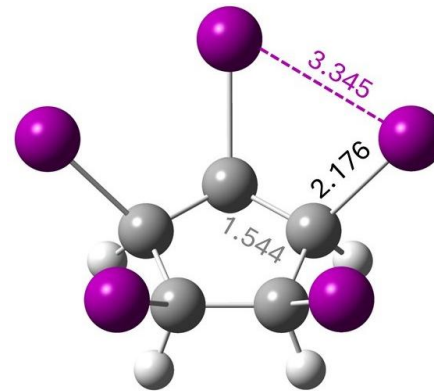
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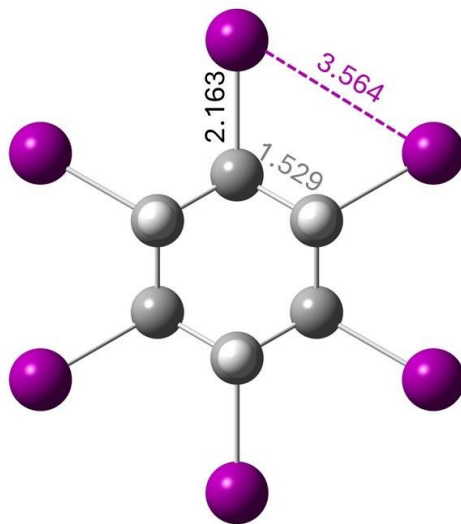
# Interatomic distances



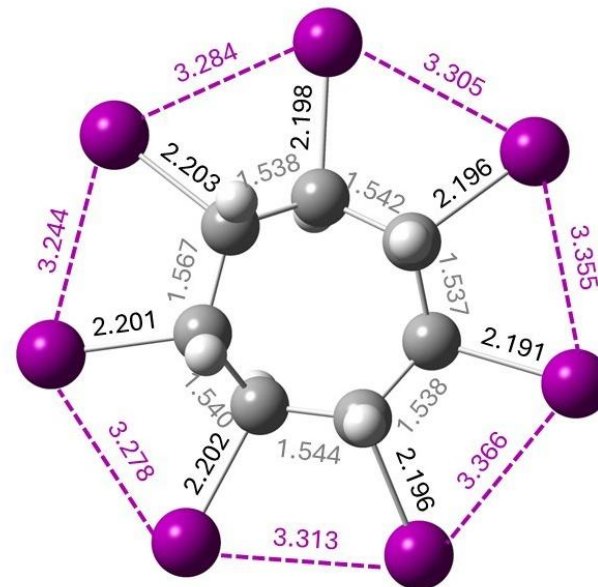
$C_4H_4I_4^{2+}$



$C_5H_5I_5^{2+}$

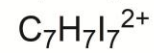
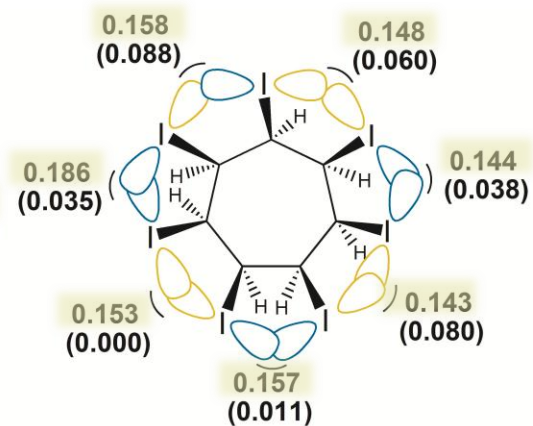
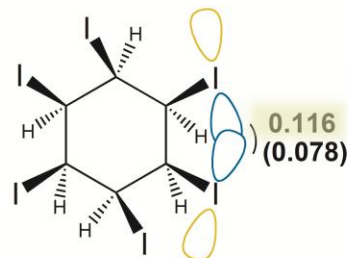
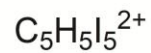
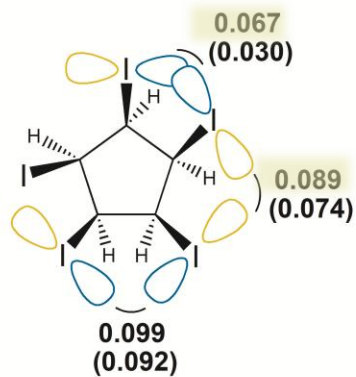
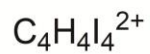
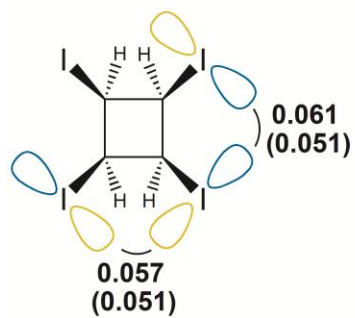


$C_6H_6I_6^{2+}$

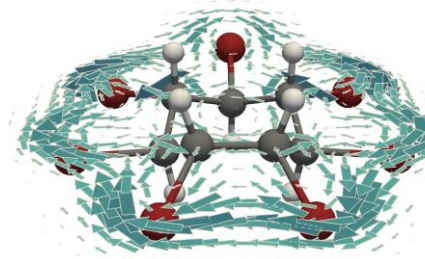
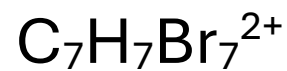
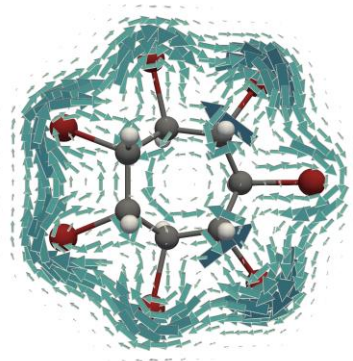
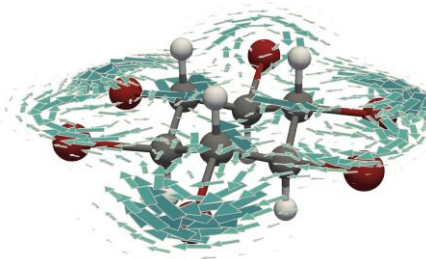
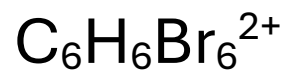
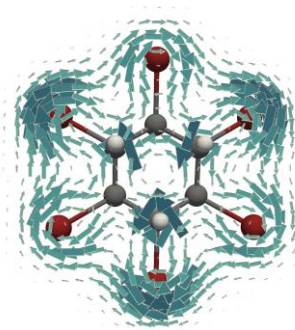
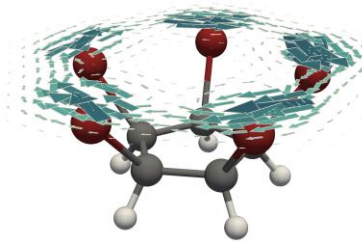
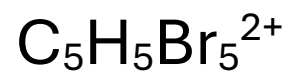
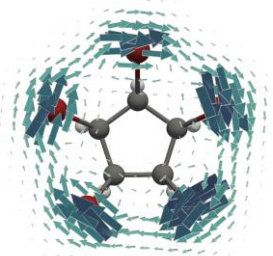
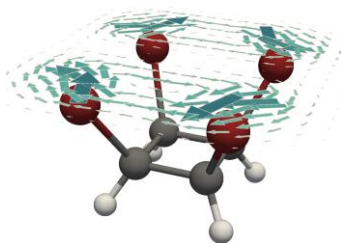
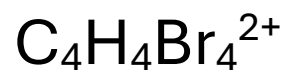
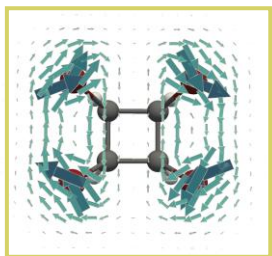


$C_7H_7I_7^{2+}$

# Overlap integrals

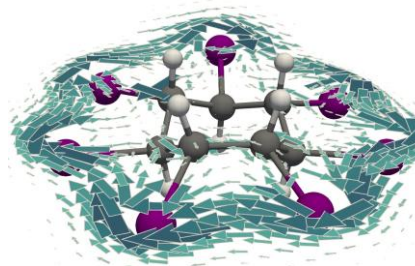
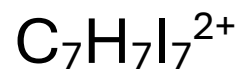
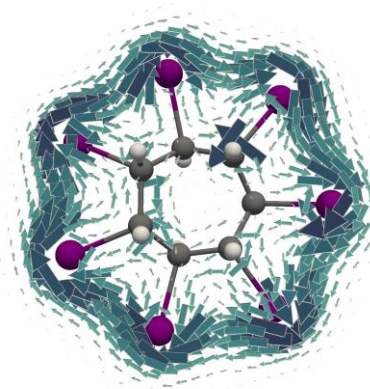
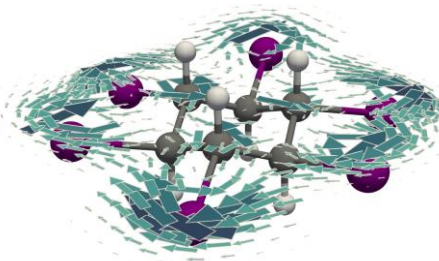
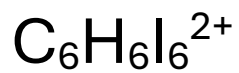
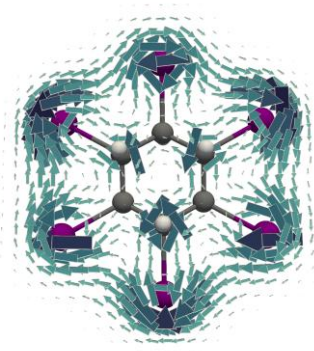
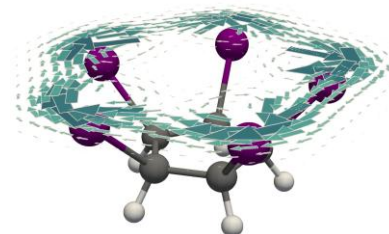
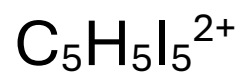
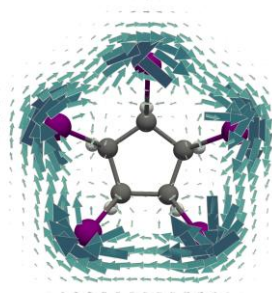
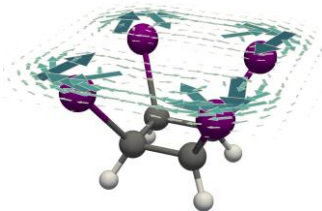
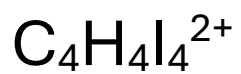
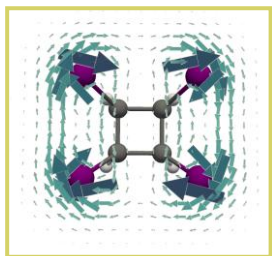


# Total current density maps



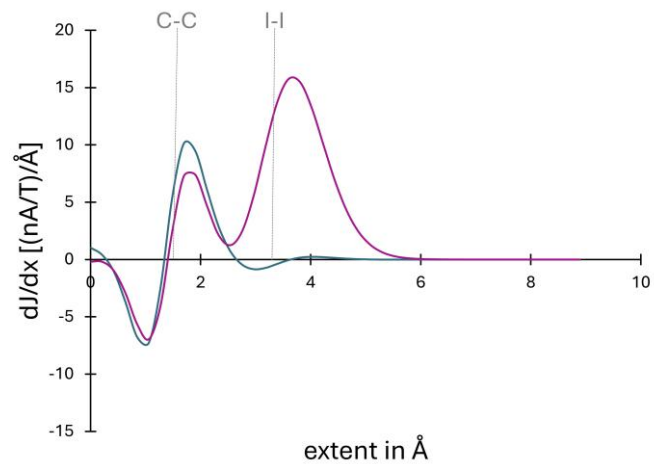
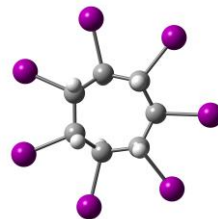
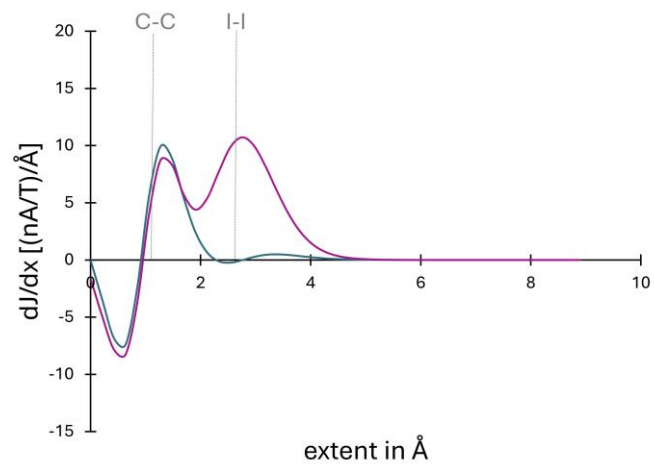
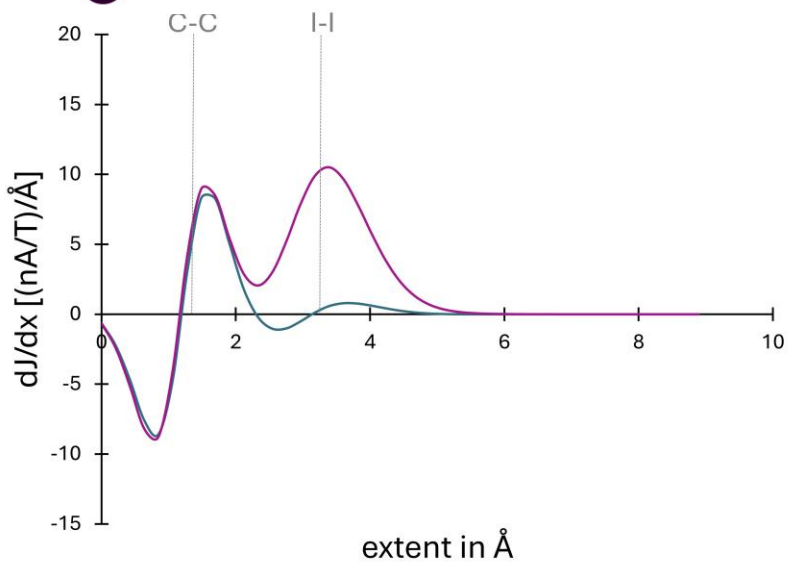
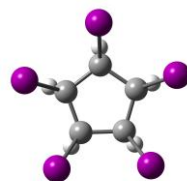
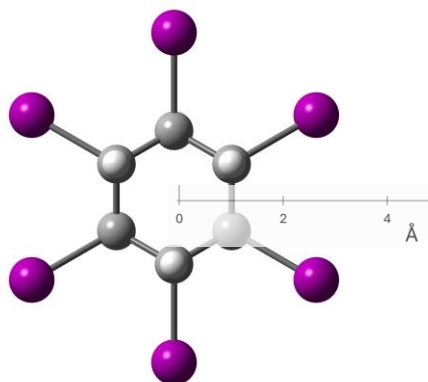
CTOCD-DZ/B3LYP/def2TZVP

# Total current density maps



CTOCD-DZ/B3LYP/def2TZVP

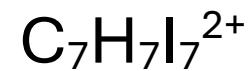
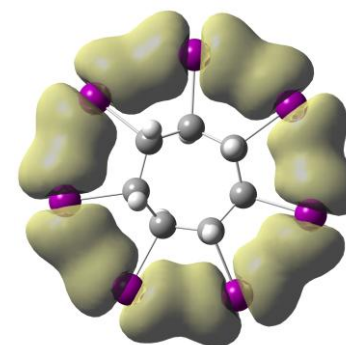
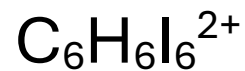
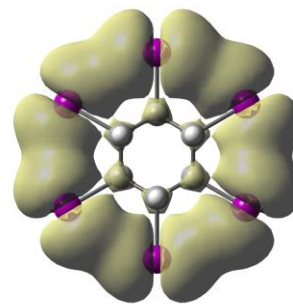
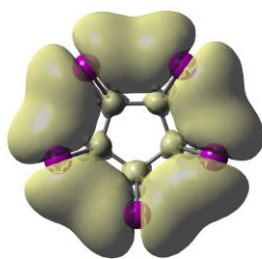
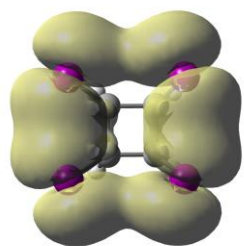
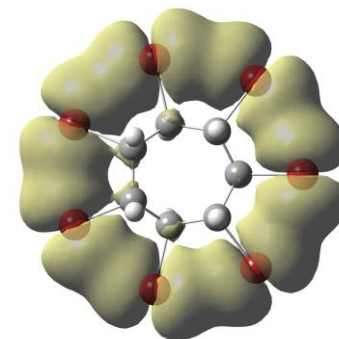
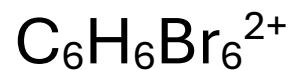
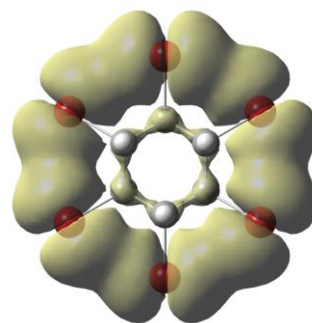
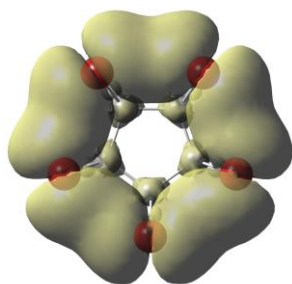
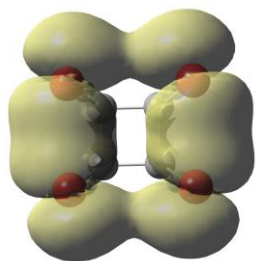
# Bond current strengths profile

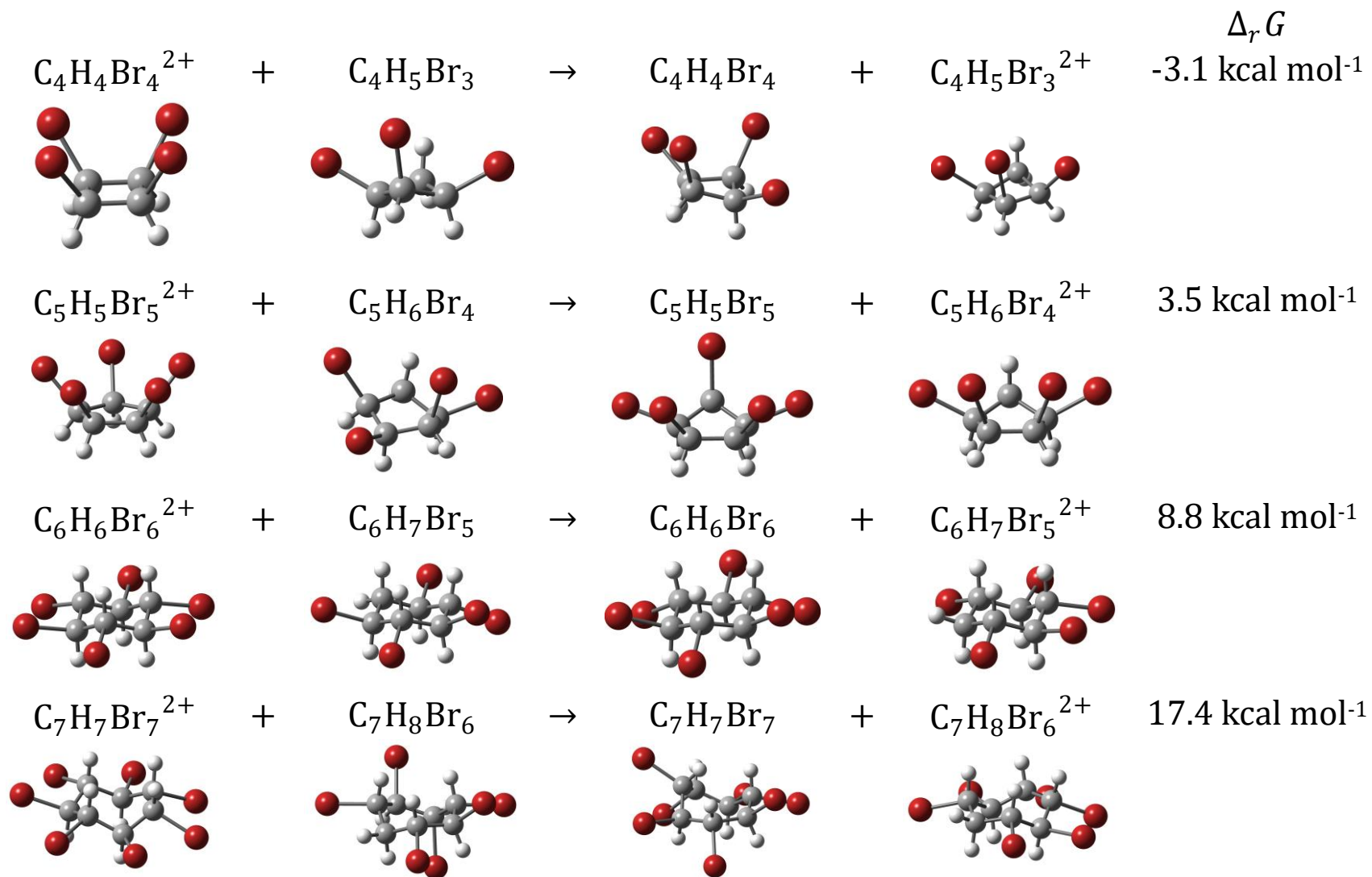


C<sub>6</sub>H<sub>6</sub>I<sub>6</sub> – plava linija

C<sub>6</sub>H<sub>6</sub>I<sub>6</sub><sup>2+</sup> – ljubičasta linija

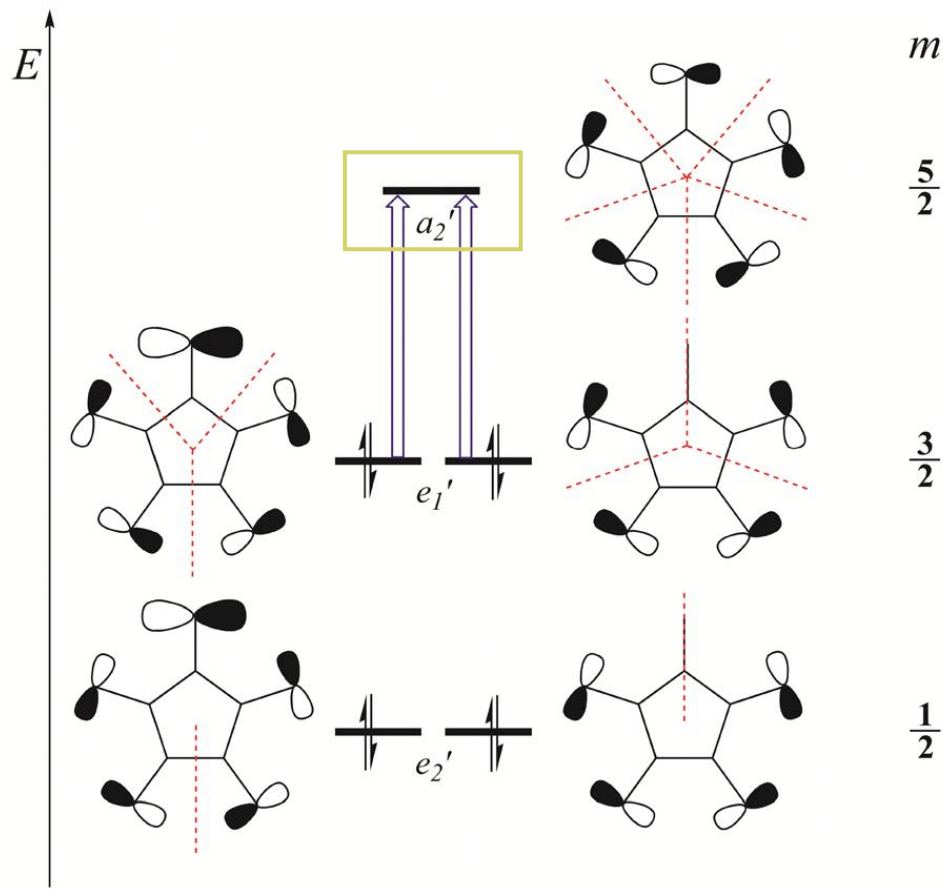
# Isosurfaces of the $\sigma$ -EDDB<sub>H</sub> function



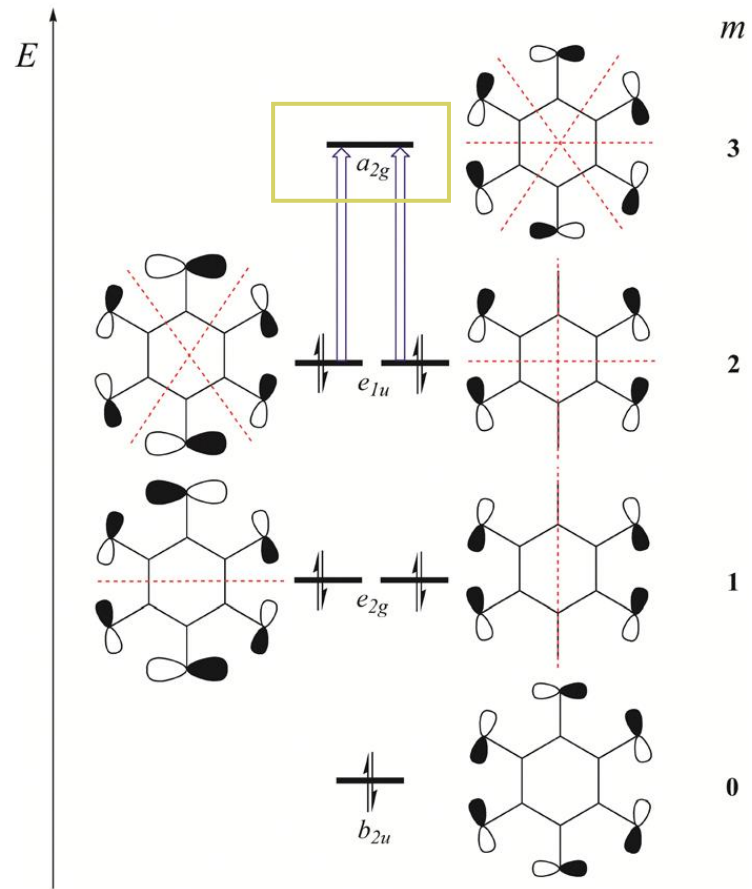


# Idealized representation of $\sigma$ -type molecular orbitals

## $D_{5h}$ symmetry



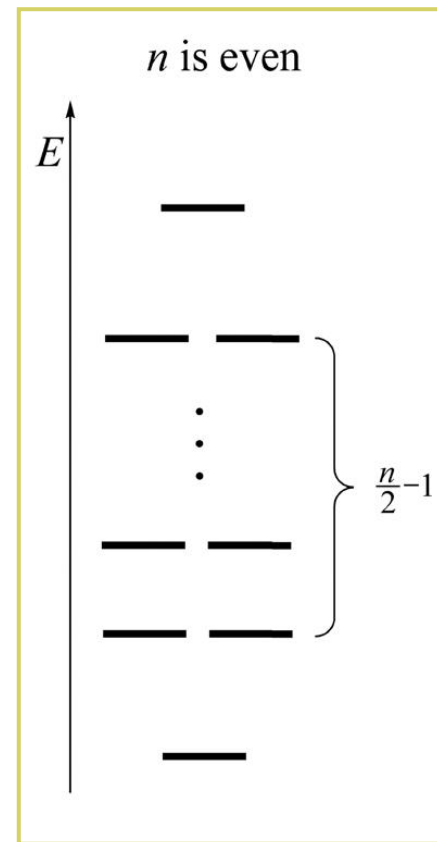
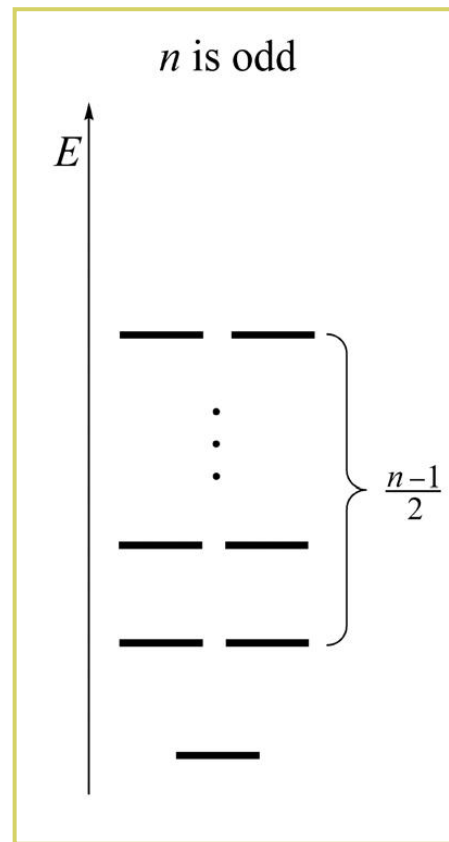
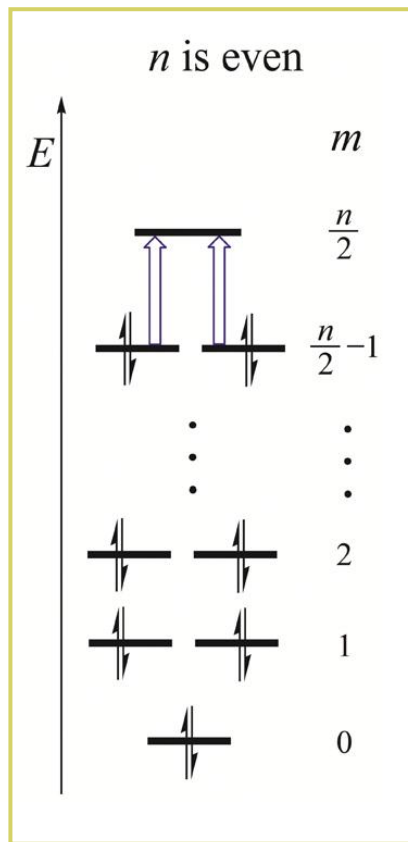
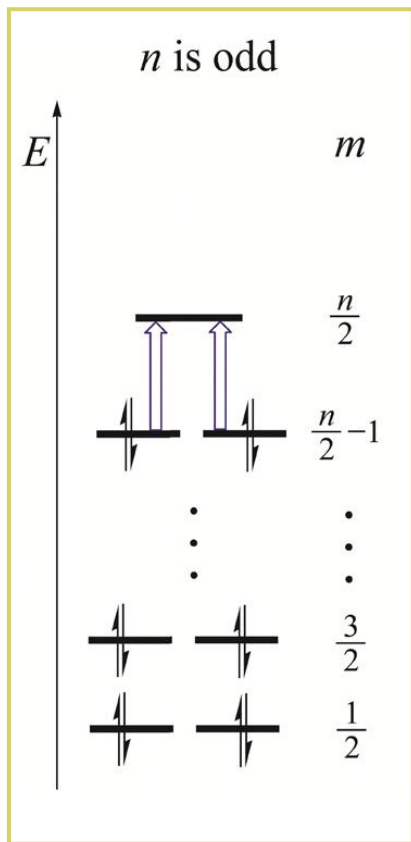
## $D_{6h}$ symmetry



# Molecular orbital diagrams

$\sigma$ -type molecular orbital energies  
in halogenated cycloalkanes

Frost–Musulin diagrams for conventional  
 $\pi$  molecular orbitals in annulenes



# Conclusions

In dicationic halogenated cycloalkanes, oxidation leads to **shorter I-I/Br-Br distances** and **planar halogen rings**, promoting  $\sigma$ -electron delocalization.

MICD reveals a clear shift from **localized currents** in neutrals to **global diatropic  $\sigma$ -currents** in dications;  
 $C_4H_4X_4^{2+}$  remains  **$\sigma$ -nonaromatic**.

$\sigma$ -aromaticity does **not always follow Hückel's rule**: it holds for **even-membered** halogen rings but breaks down in **odd-membered** ones.