Ring currents in *peri*odo-hydrocarbons

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Introduction

- Double aromaticity – aromaticity composed of two circularly delocalized orbitals.[‡]

[‡] J. Chandrasekhar, E. D. Jemmis. P. v. R. Schleyer, *Tetrahedron Letters*, 1979, 20, 39, 3707-3710

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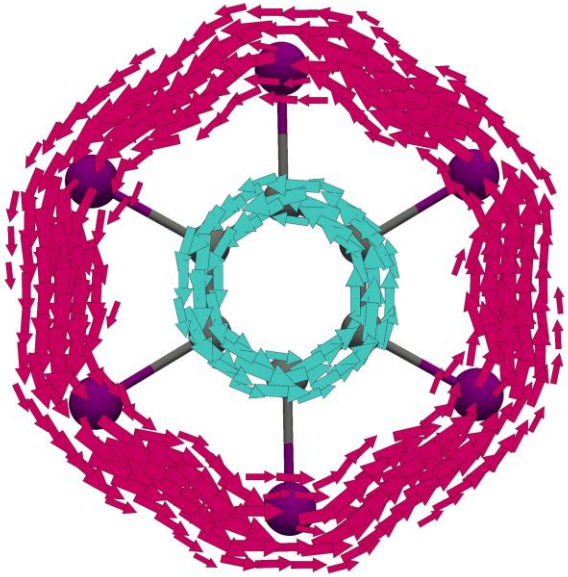
- Double aromaticity in halogen substituted benzene dications derivatives has been extensively investigated.*



* I. Ciofini, P. P. Lainé and C. Adamo, *Chem Phys Lett*, 2007, 435, 171–175;
R. W. A. Havenith, P. W. Fowler, S. Fias and P. Bultinck, *Tetrahedron Lett*, 2008, 49, 1421–1424;
M. Orozco-Ic, J. Barroso, R. Islas and G. Merino, *ChemistryOpen*, 2020, 9, 657–661.

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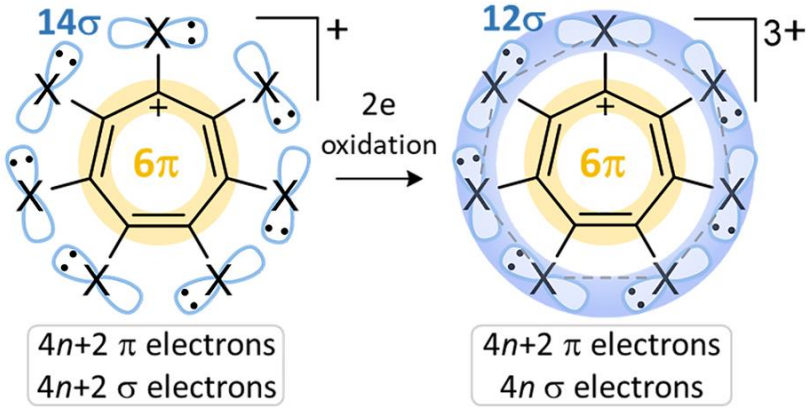

S. Escayola, N. Proos Vedin, A. Poater, H. Ottosson and M. Solà, *J Phys Org Chem*, 2023, 36, e4447. P. W. Fowler and R. W. A. Havenith, *J Phys Chem A*, 2021, 125, 6374–6383.

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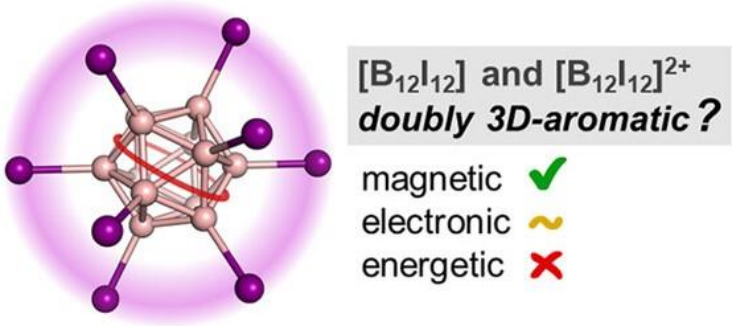
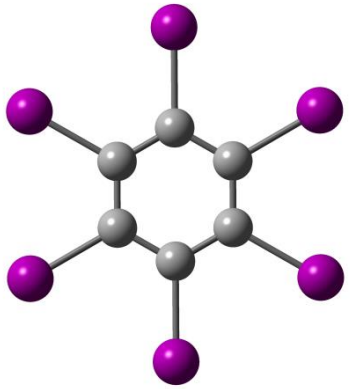
- Double (anti)aromatic character is later investigated in halogen substituents of the tropylium cations and the cyclooctatetraene cations.#
- Possibility of double 3D-aromaticity is analysed in $[B_{12}I_{12}]$ and $[B_{12}I_{12}]^{2+}$. §

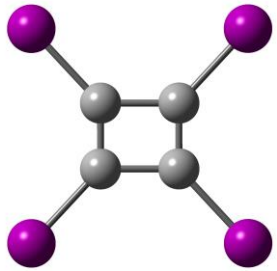


§ J. Poater, S. Escayola, A. Poater, F. Teixidor, H. Ottosson, C. Viñas and M. Solà, *J Am Chem Soc*, 2023, 145, 22527–22538.

Studied molecules

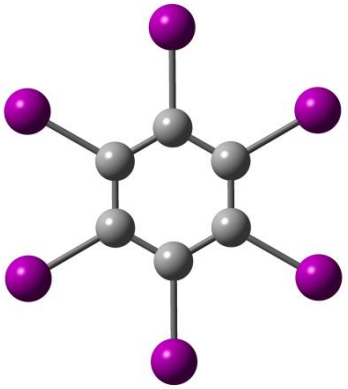


C_6I_6



C_4I_4

Studied molecules



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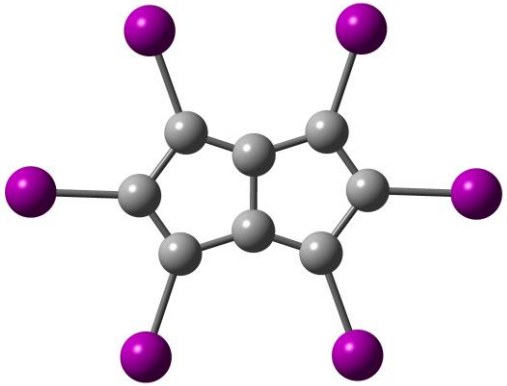
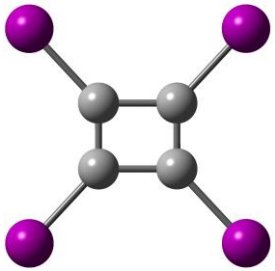


C_8I_6



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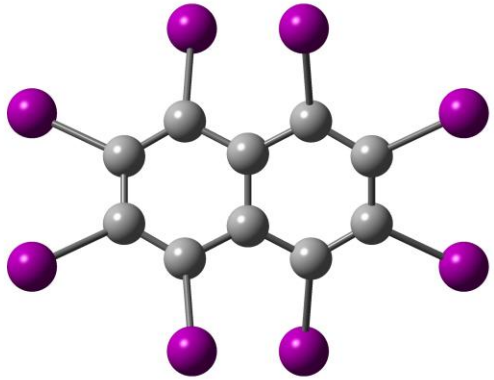
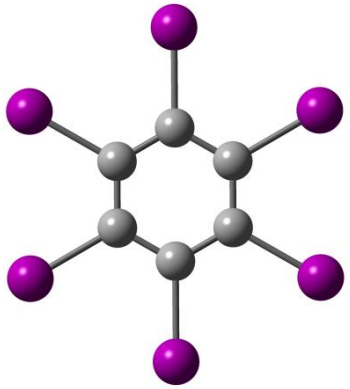


$C_{10}I_8$

Studied molecules



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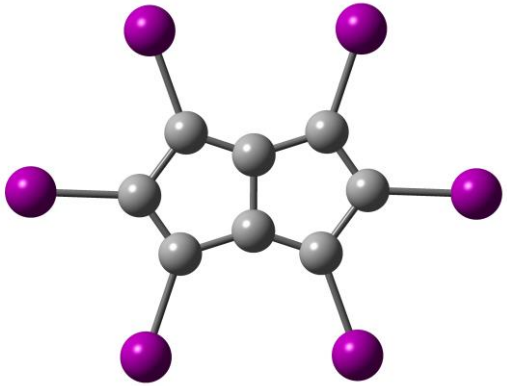

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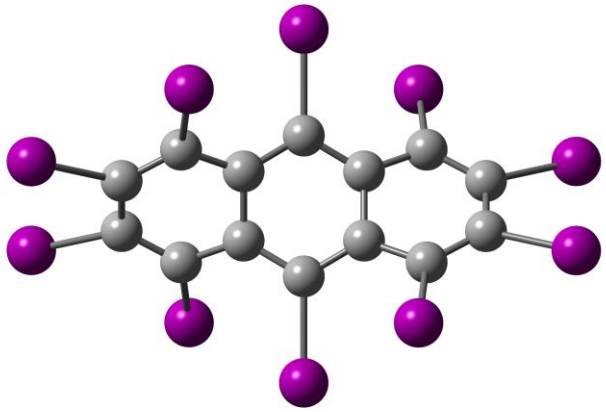
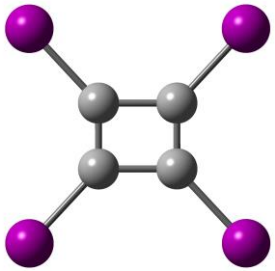


$C_{14}I_{10}$



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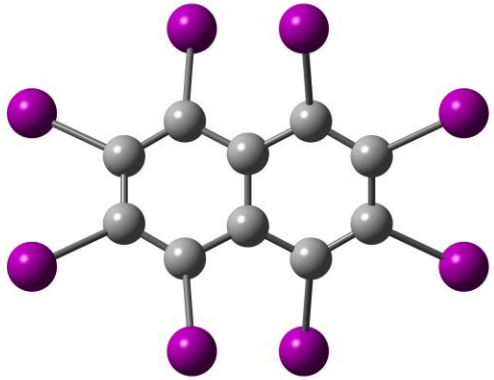

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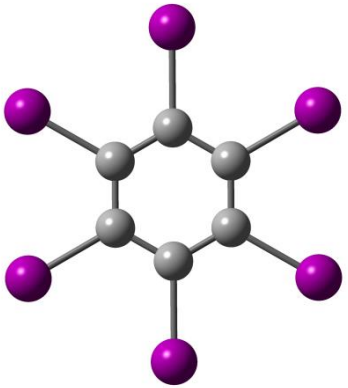

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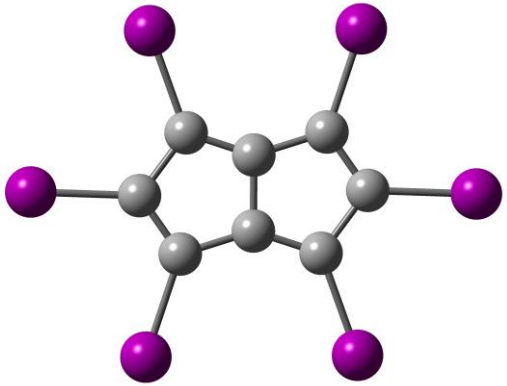

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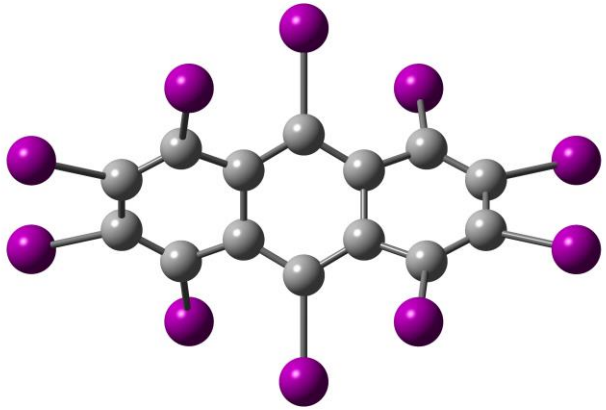

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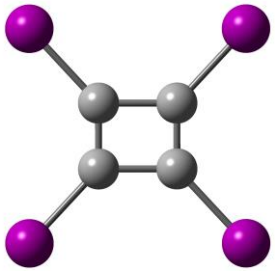

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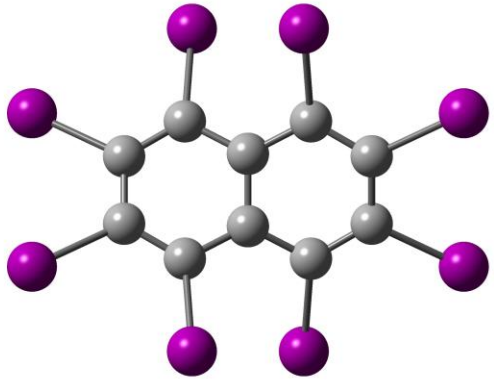

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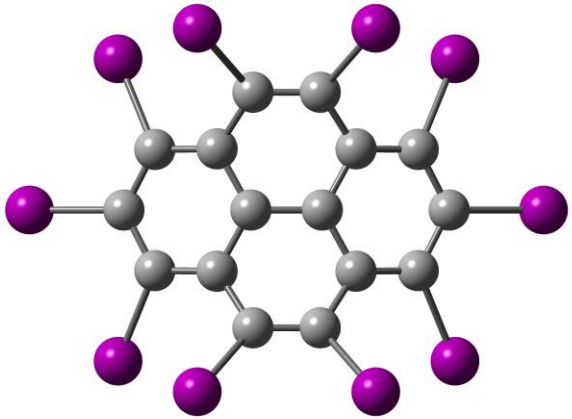

$C_{16}I_{10}$

Computational details

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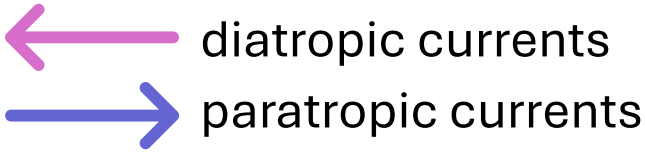

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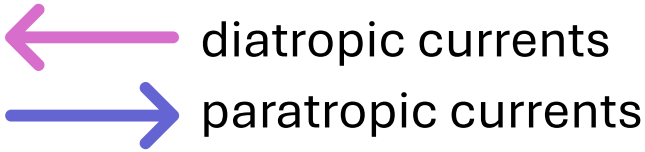

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  ← diatropic currents

  → paratropic currents
- EDDB indices were computed using available software.
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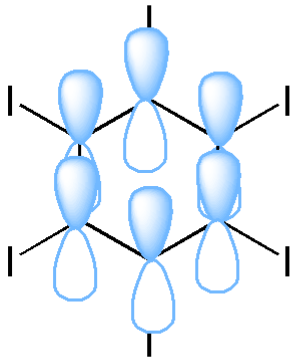
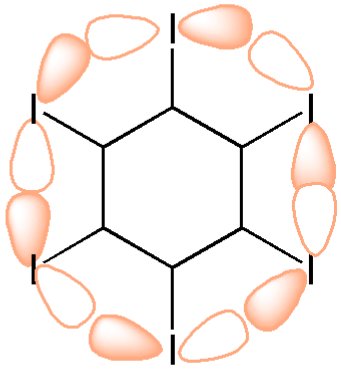
*Per*iodo-benzene – σ and π notations



π orbitals



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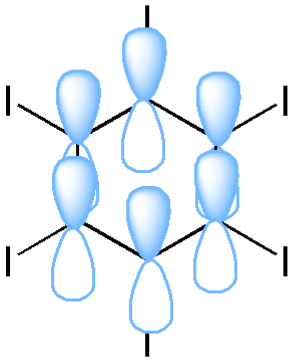

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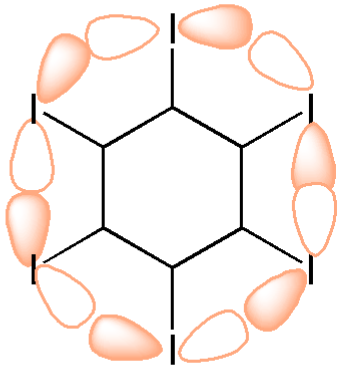

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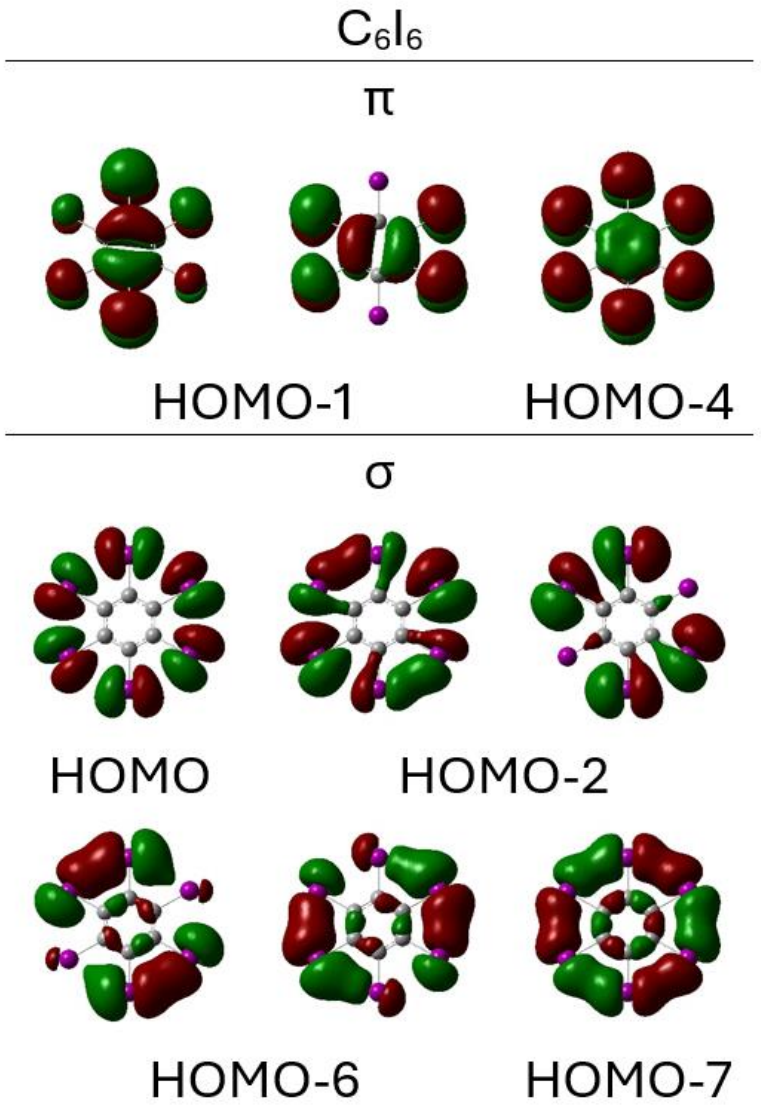
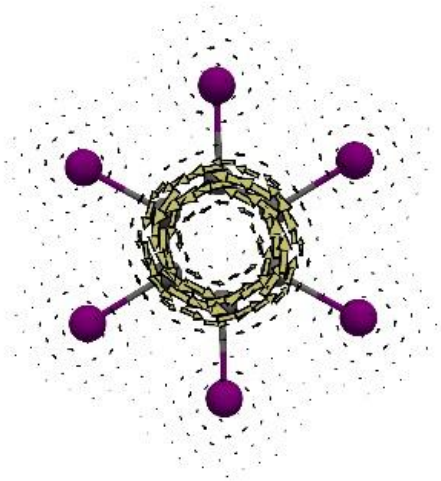


*Per*iodo-benzene

C_6I_6

π-currents



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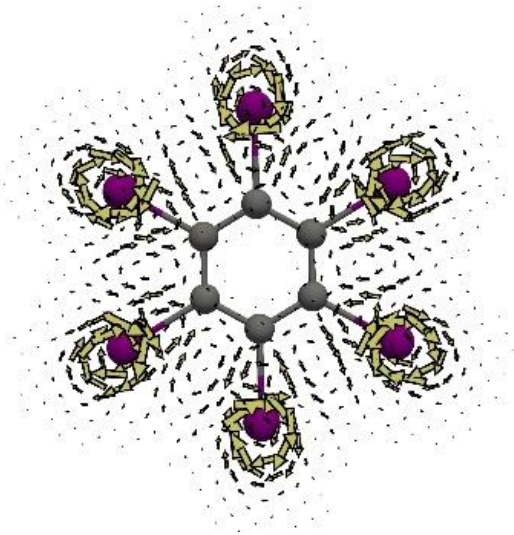

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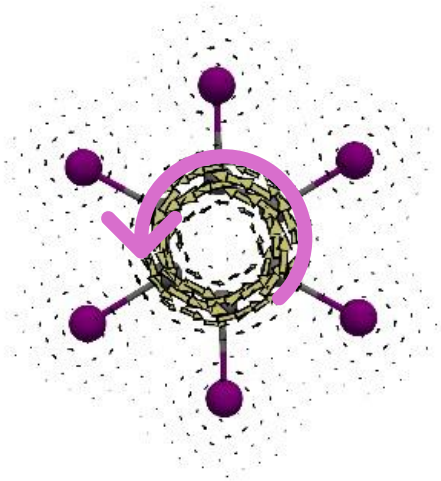

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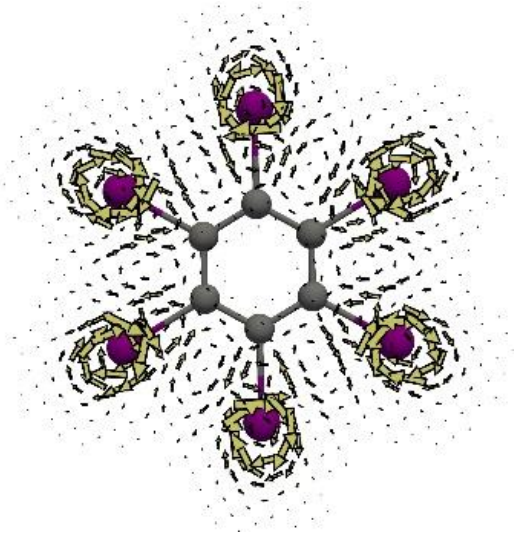

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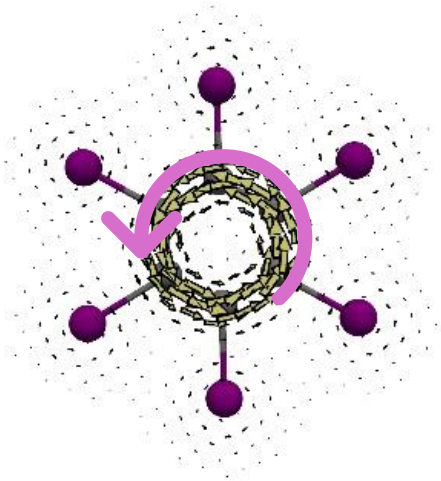
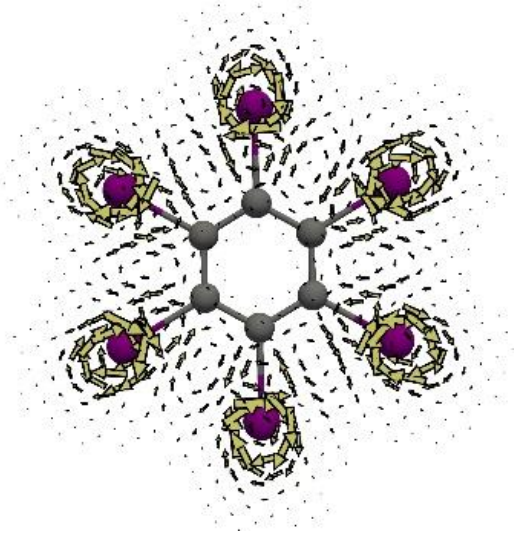
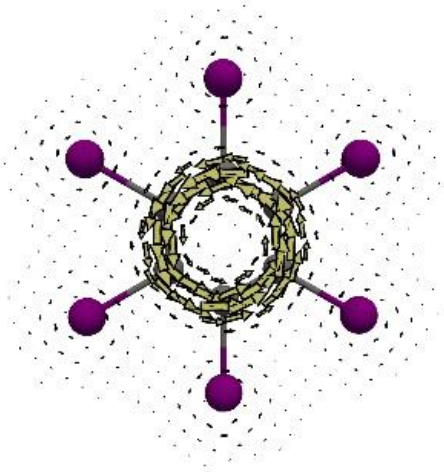
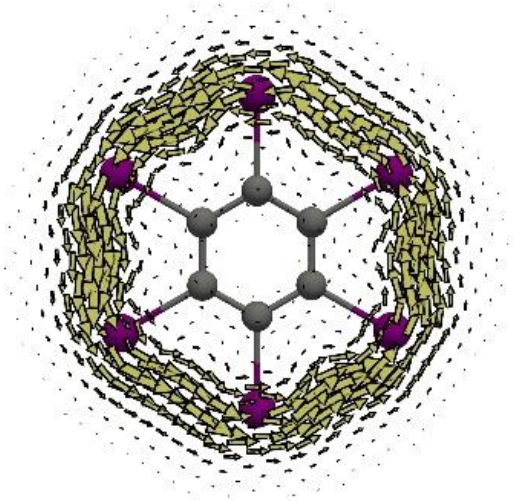




$C_6I_6^{2+}$





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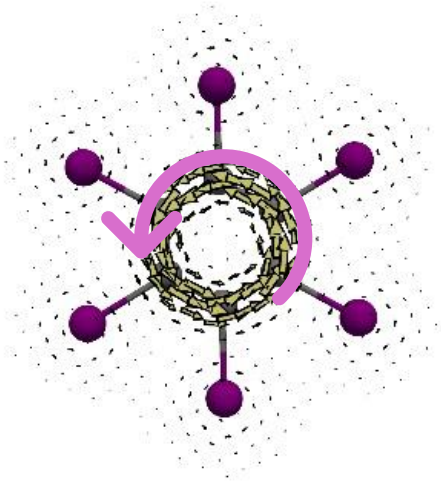

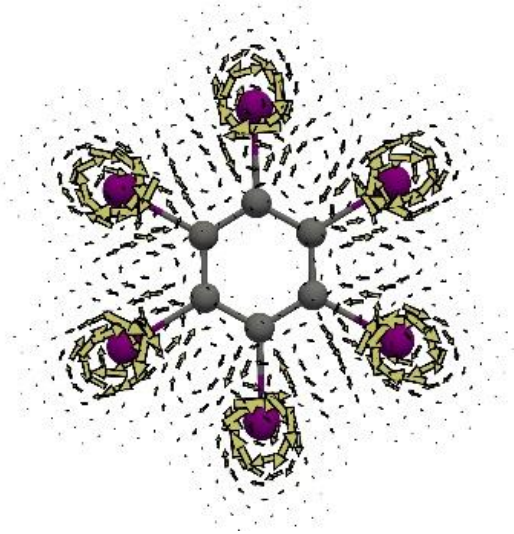

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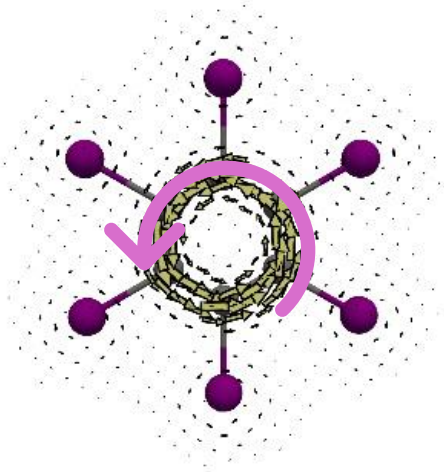

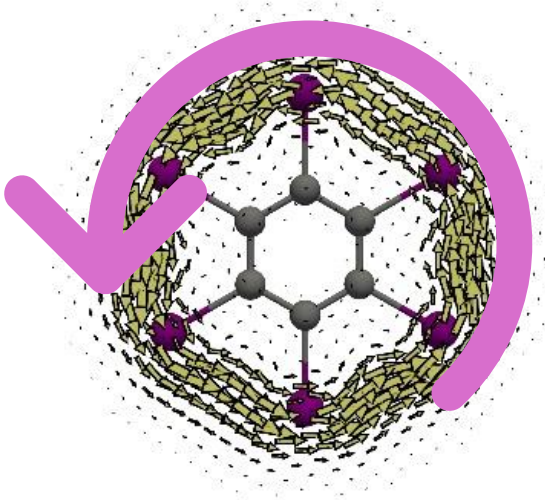

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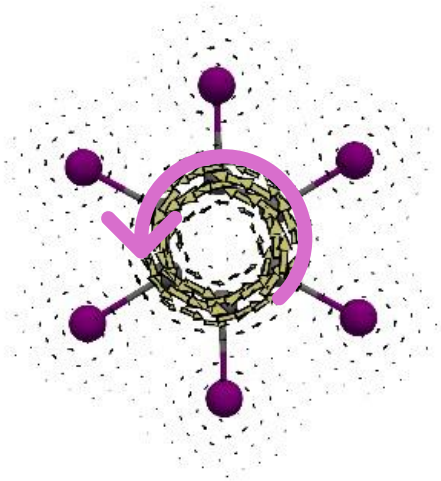
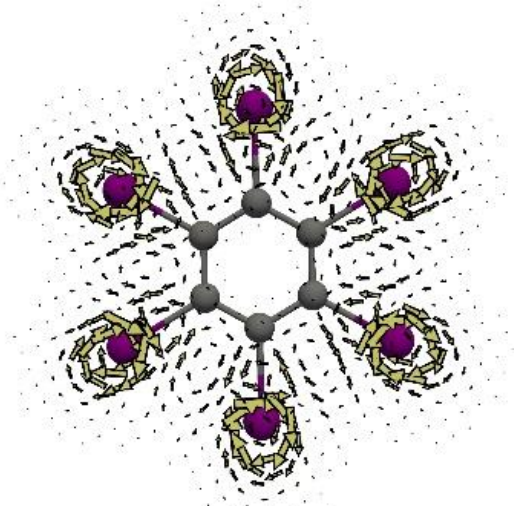
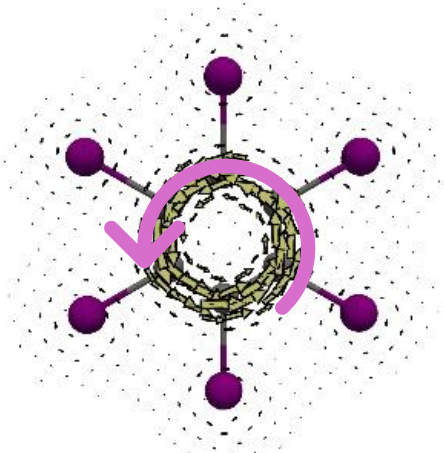


6 electrons



12 electrons

$C_6I_6^{2+}$



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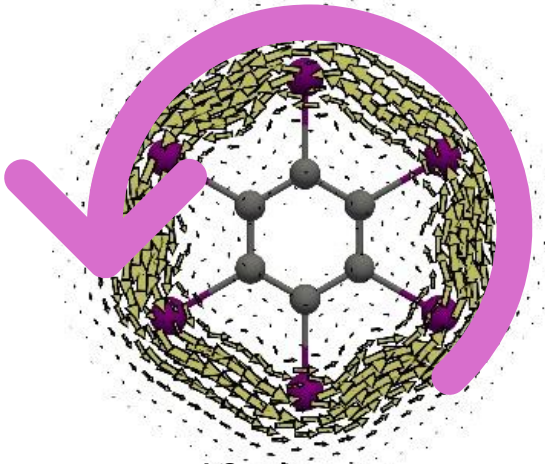
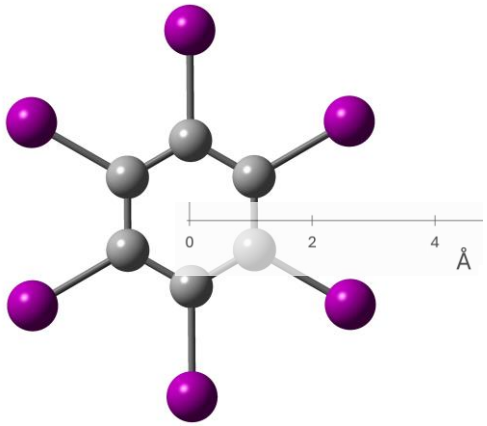


10 electrons

*Per*iodo-benzene – bond current strengths profile



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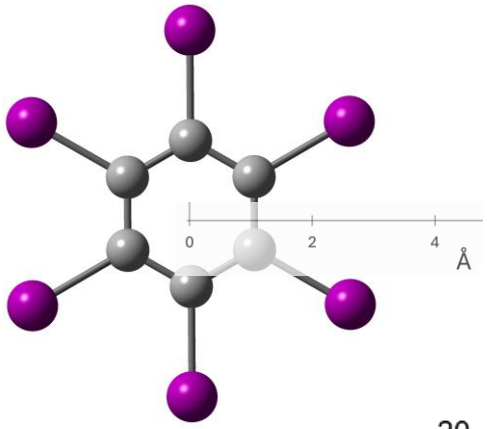

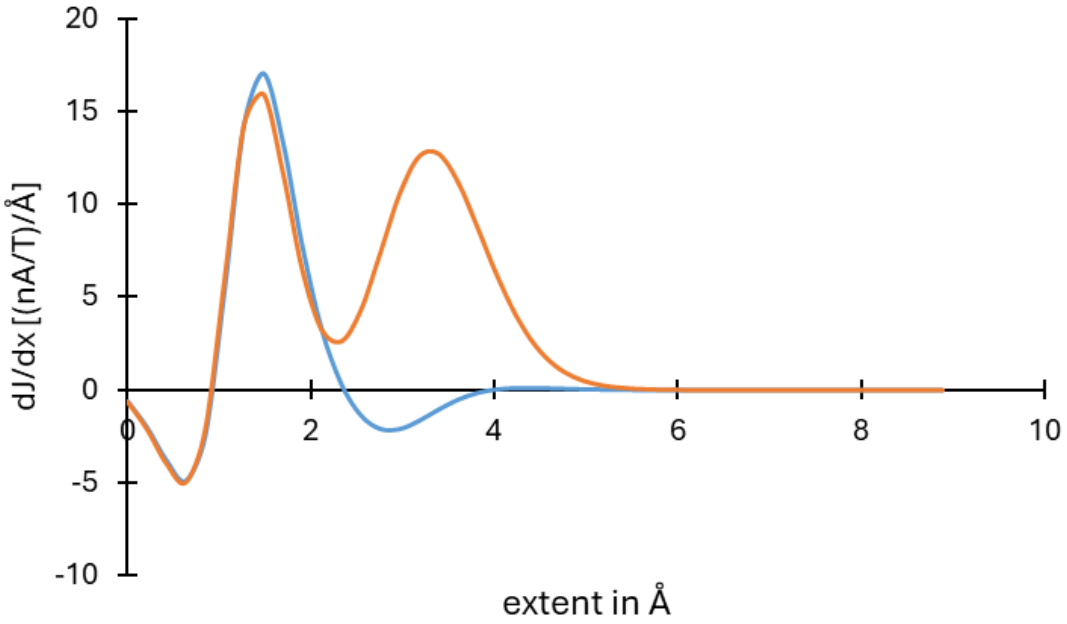

C_6I_6 – blue line

$C_6I_6^{2+}$ - orange line

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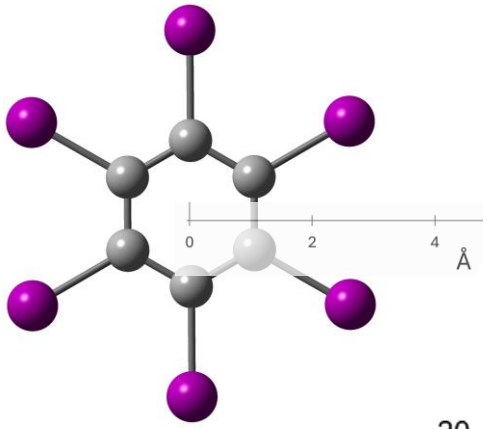
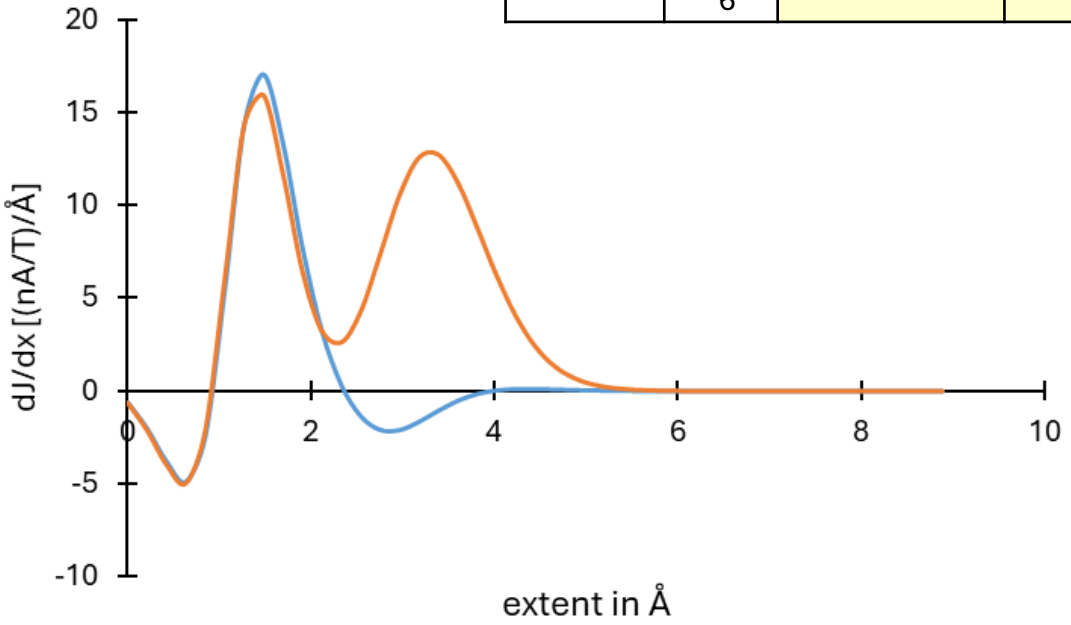


		J [nA T^{-1}]	EDDB	I_{ring}
C_6I_6	C_6	9.4	5.074	0.625
	I_6	-1.0	0.227	0.065
$C_6I_6^{2+}$	C_6	8.6	5.038	0.622
	I_6	18.7	5.333	0.319



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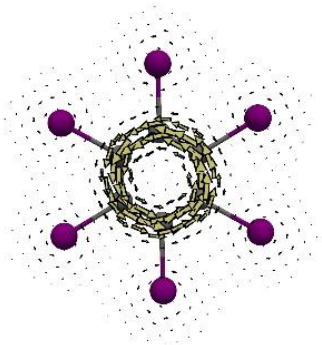
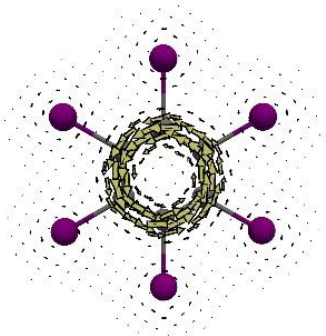
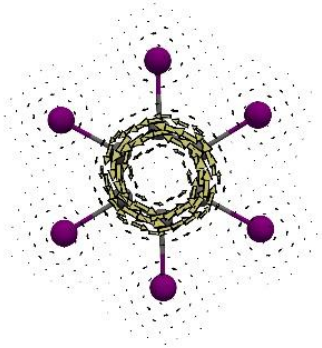


C_6I_6

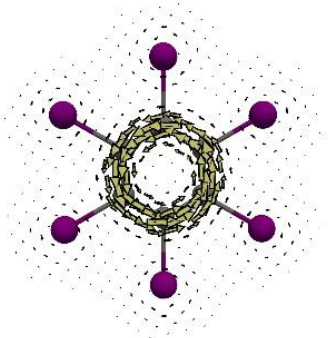


$C_6I_6^{2+}$

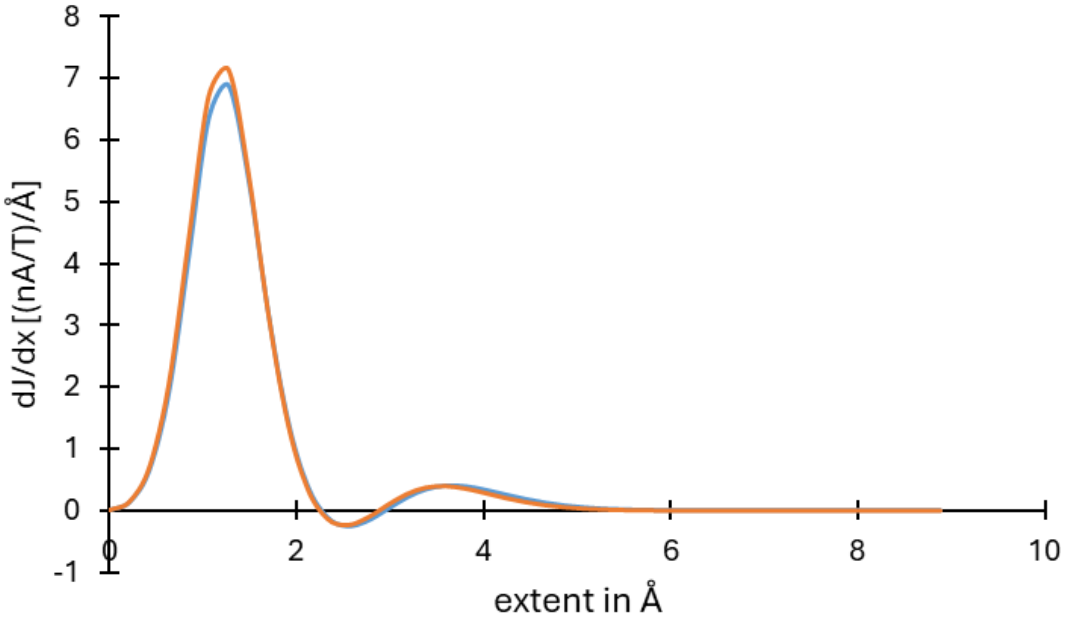
*Per*iodo-benzene – π bond current strengths profile



C_6I_6



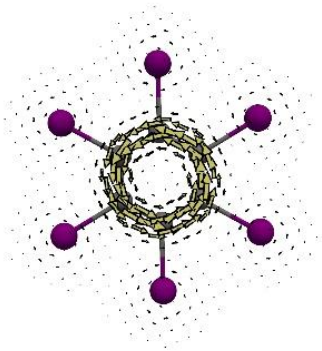
$C_6I_6^{2+}$



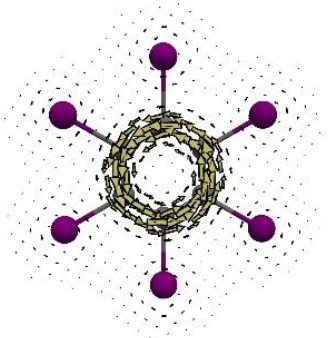
C_6I_6 – blue line

$C_6I_6^{2+}$ - orange line

*Per*iodo-benzene – π bond current strengths profile

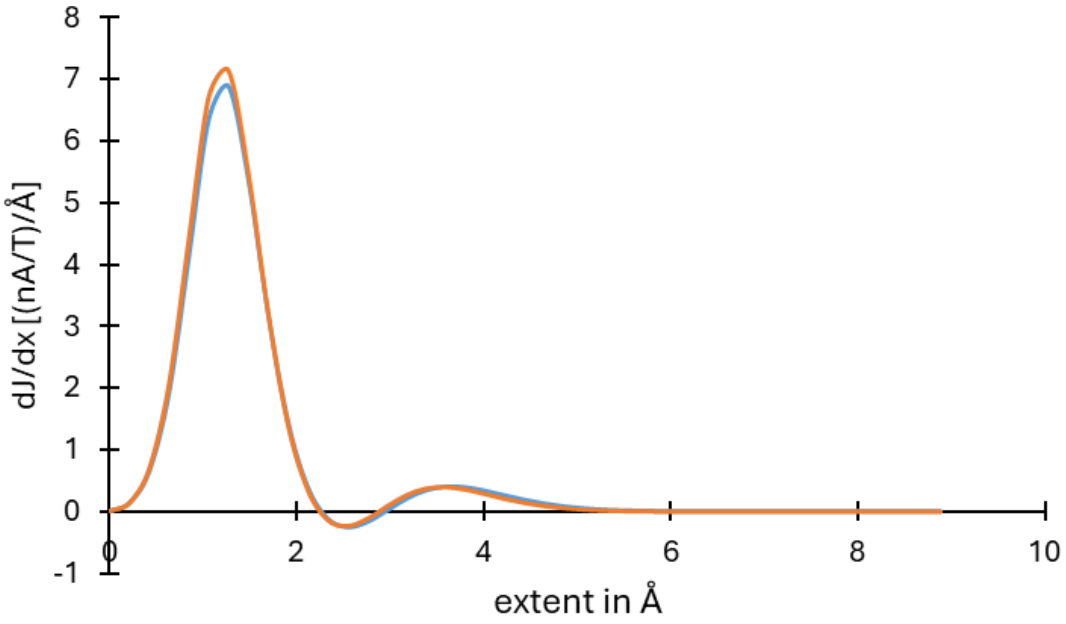


C_6I_6



$C_6I_6^{2+}$

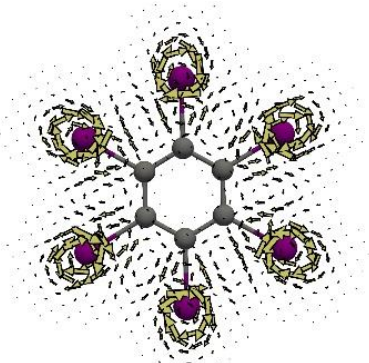
	J^{π} [nA T^{-1}]	$EDDB_{\pi}$
C_6I_6	6.4	5.737
$C_6I_6^{2+}$	6.6	5.733



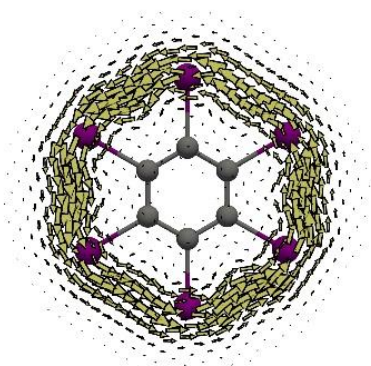
C_6I_6 – blue line

$C_6I_6^{2+}$ - orange line

*Per*iodo-benzene – σ bond current strengths profile

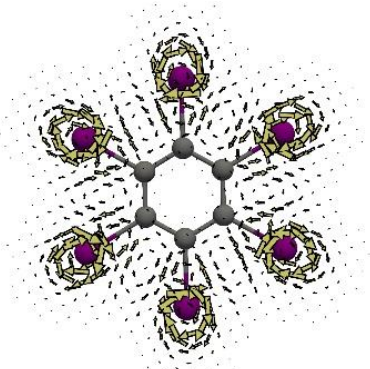


C_6I_6

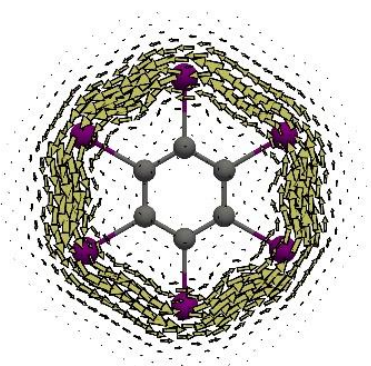


$C_6I_6^{2+}$

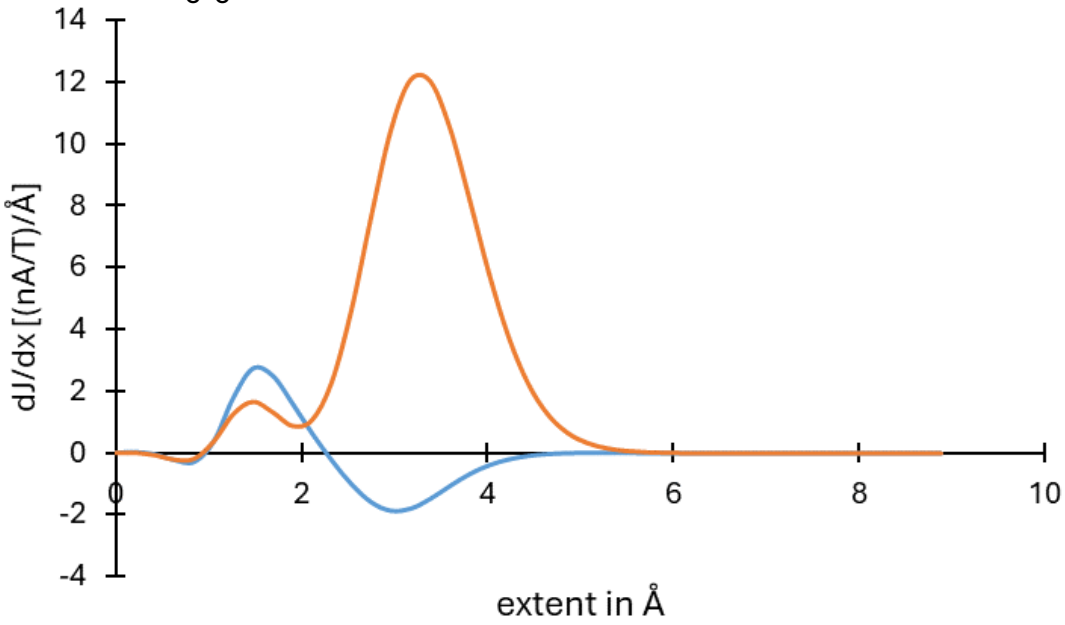
*Per*iodo-benzene – σ bond current strengths profile



C_6I_6



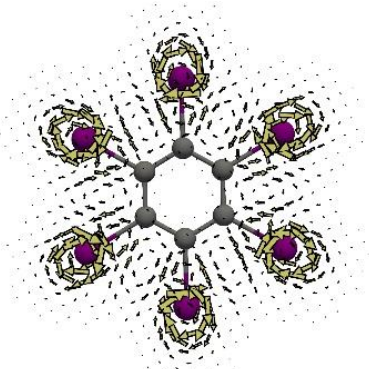
$C_6I_6^{2+}$



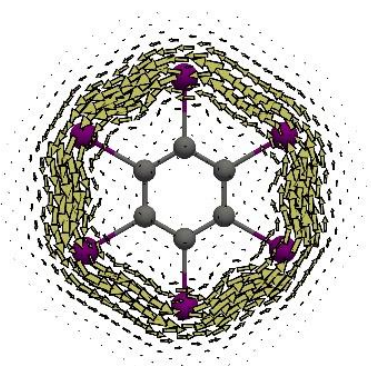
C_6I_6 – blue line

$C_6I_6^{2+}$ - orange line

*Per*iodo-benzene – σ bond current strengths profile

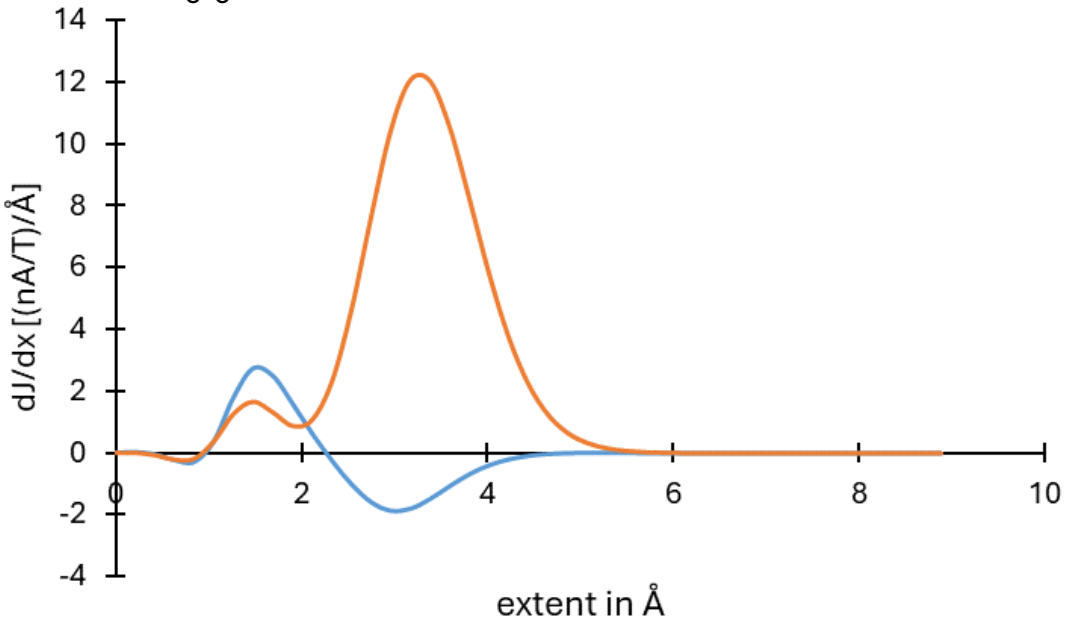


C_6I_6



$C_6I_6^{2+}$

	J^{σ} [nA T^{-1}]	$EDDB_{\sigma}$
C_6I_6	-2.0	0.623
$C_6I_6^{2+}$	17.6	5.812



C_6I_6 – blue line

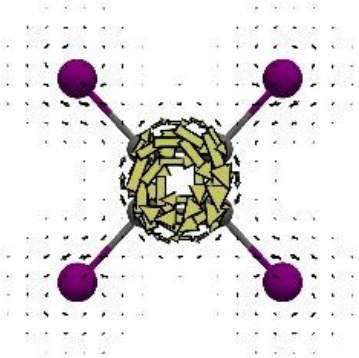
$C_6I_6^{2+}$ - orange line

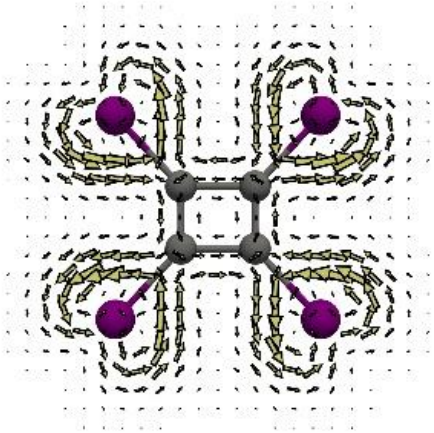
*Per*iodo-cyclobutadiene

π-currents

σ-currents

C_4I_4

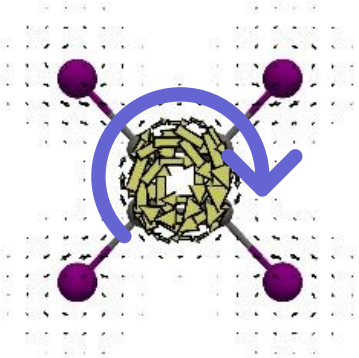




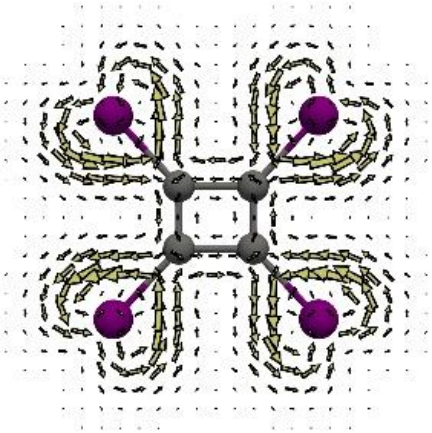
*Per*iodo-cyclobutadiene

C_4I_4

π-currents



σ-currents

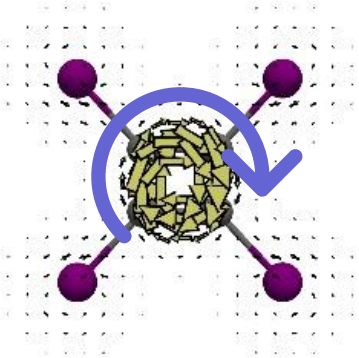


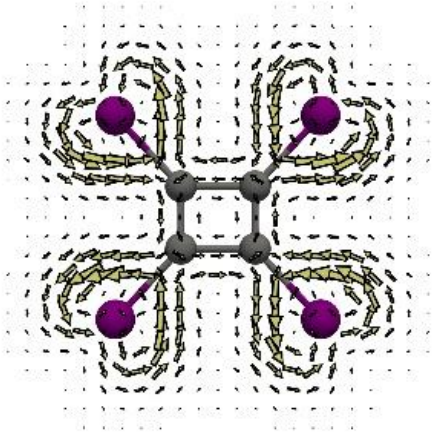
*Per*iodo-cyclobutadiene

π-currents

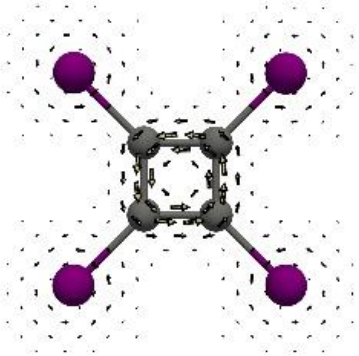
σ-currents

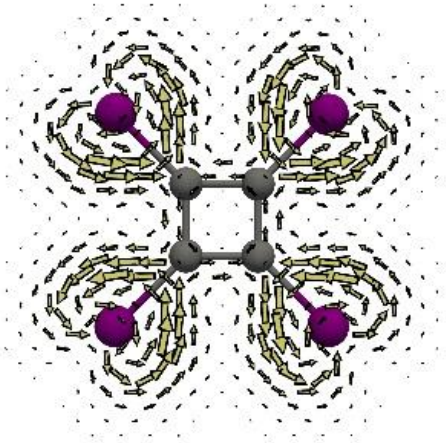
C_4I_4





$C_4I_4^{2+}$



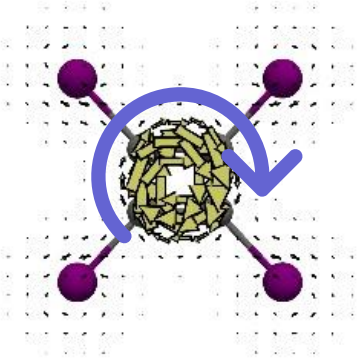


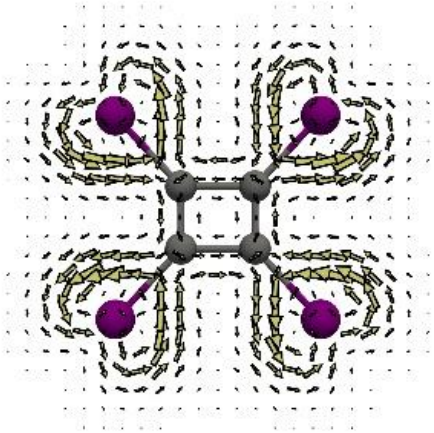
*Per*iodo-cyclobutadiene

π-currents

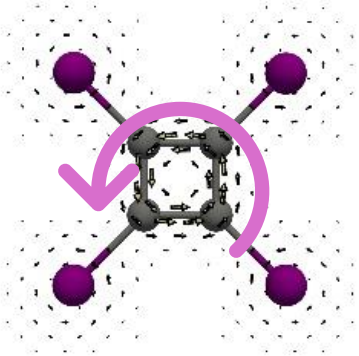
σ-currents

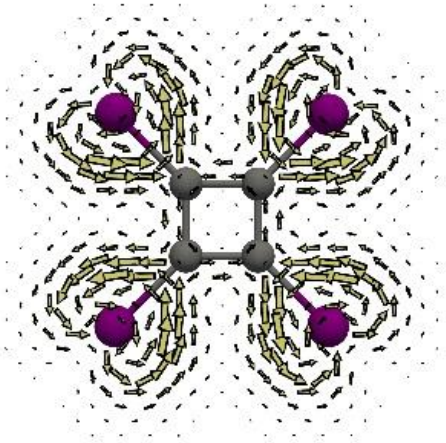
C_4I_4



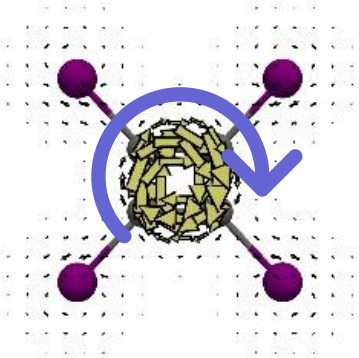
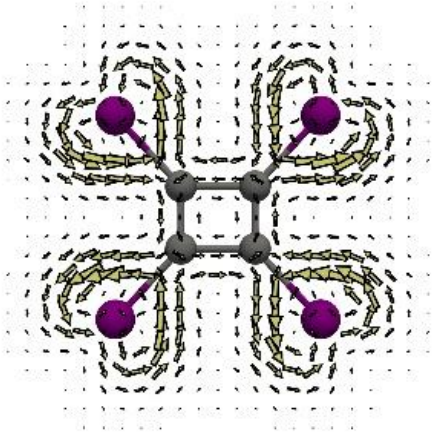
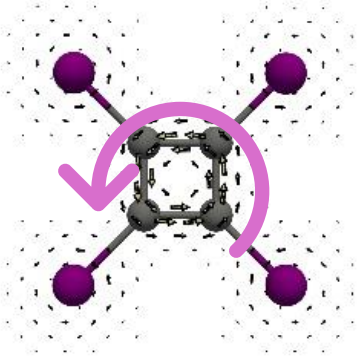
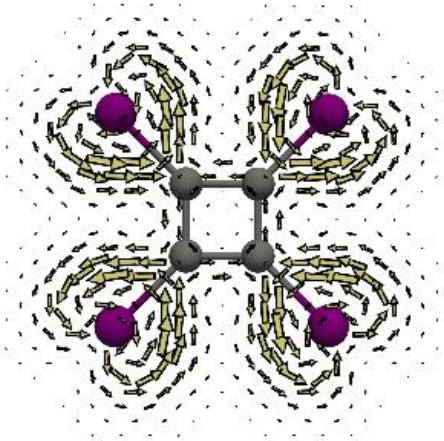


$C_4I_4^{2+}$

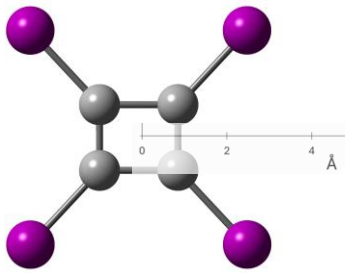


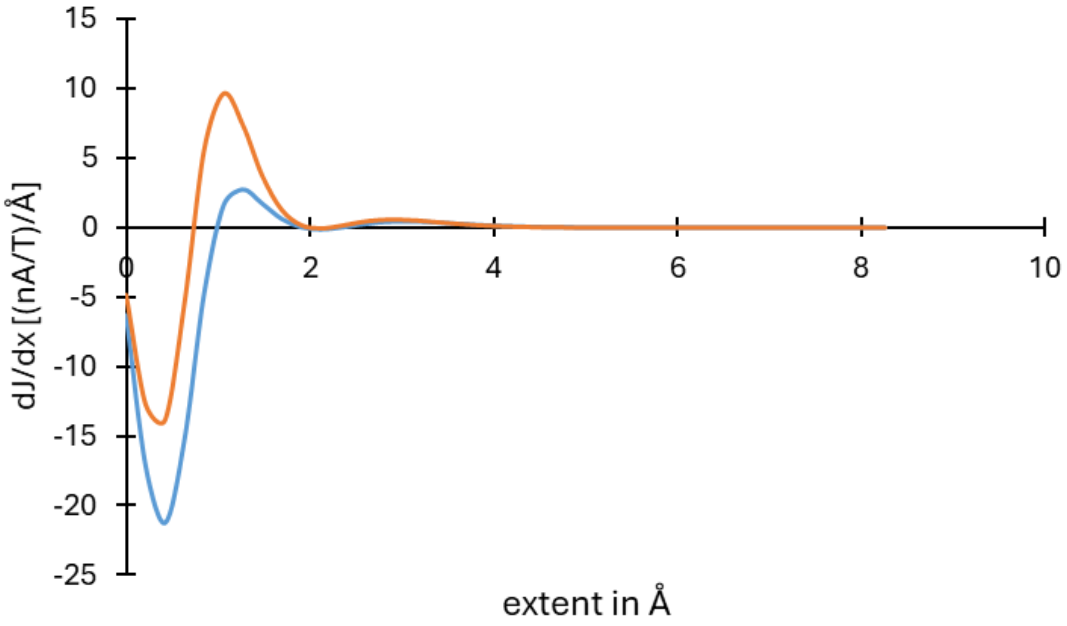


*Per*iodo-cyclobutadiene

	π-currents	σ-currents
C_4I_4		
	4 electrons	8 electrons
$C_4I_4^{2+}$		
	2 electrons	8 electrons

*Per*iodo-cyclobutadiene – bond current strengths profile

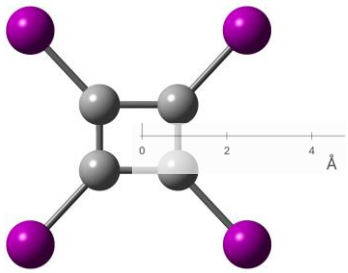




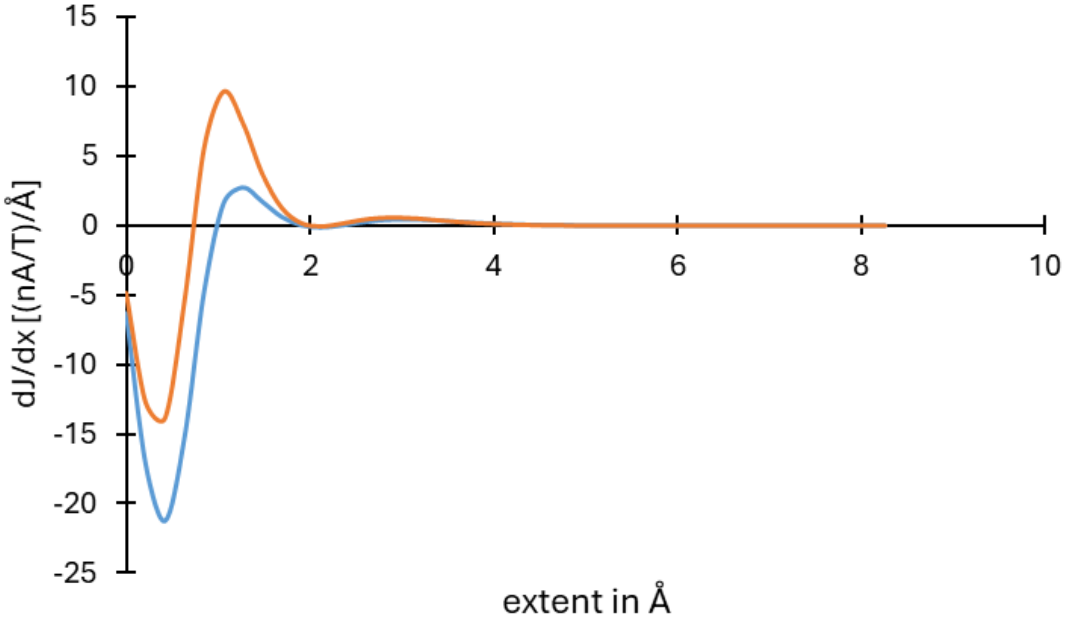
C_4I_4 – blue line

$C_4I_4^{2+}$ - orange line

*Per*iodo-cyclobutadiene – bond current strengths profile



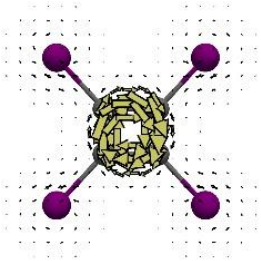
		J [nA T^{-1}]	EDDB	I_{ring}
C_4I_4	C_4	-12.3	0.211	0.217
	I_4	0.5	0.073	0.072
$C_4I_4^{2+}$	C_4	-1.9	1.225	0.453
	I_4	0.6	0.064	0.050



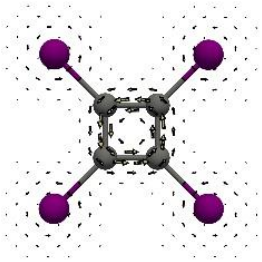
C_4I_4 – blue line

$C_4I_4^{2+}$ - orange line

*Per*iodo-cyclobutadiene – π bond current strengths profile

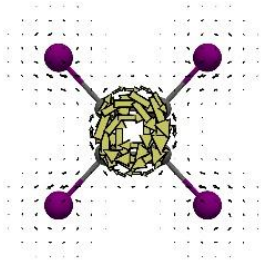


C_4I_4

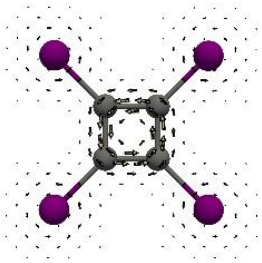


$C_4I_4^{2+}$

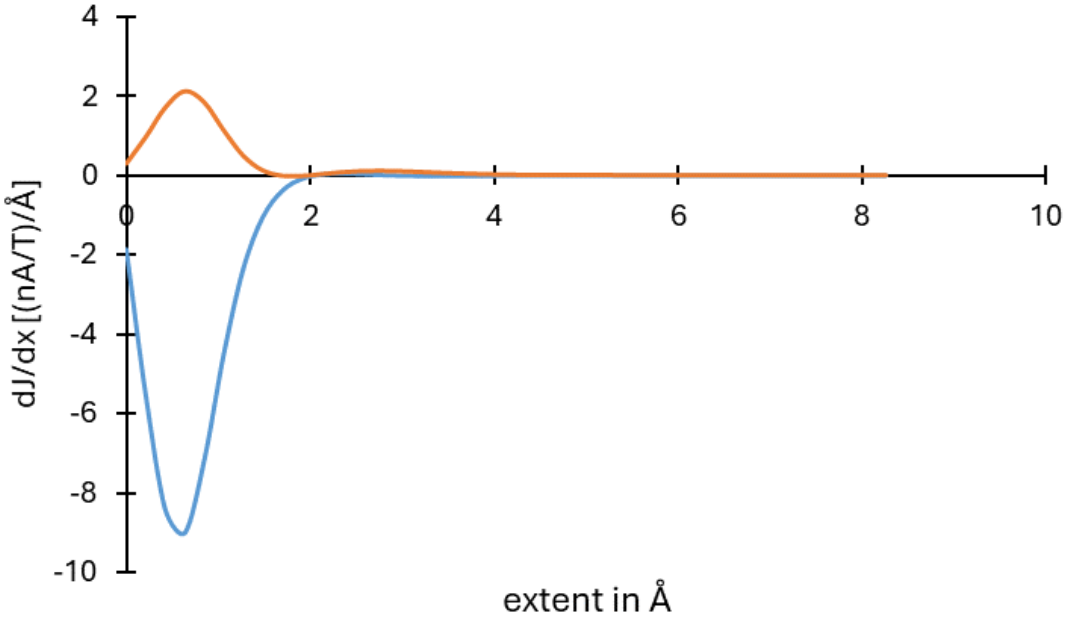
*Per*iodo-cyclobutadiene – π bond current strengths profile



C_4I_4



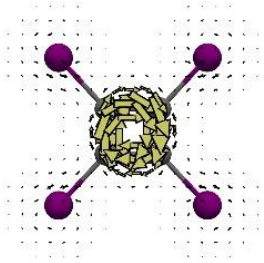
$C_4I_4^{2+}$



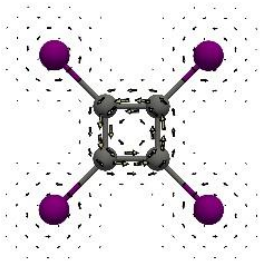
C_4I_4 – blue line

$C_4I_4^{2+}$ - orange line

*Per*iodo-cyclobutadiene – π bond current strengths profile

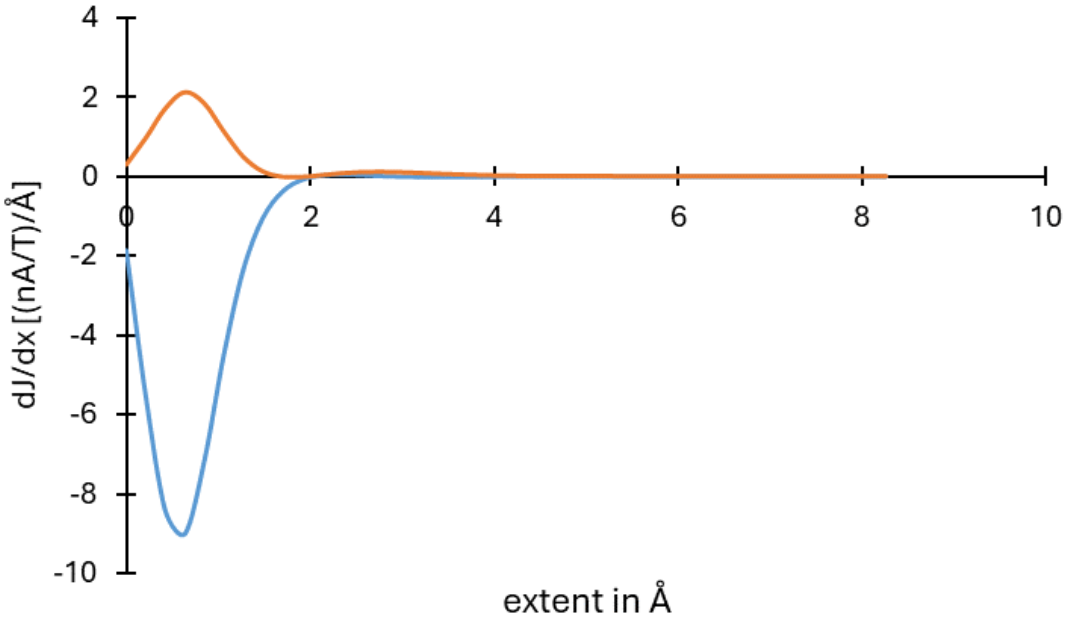


C_4I_4



$C_4I_4^{2+}$

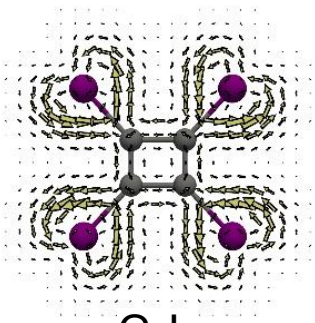
	J^{π} [nA T^{-1}]	$EDDB_{\pi}$
C_4I_4	-8.6	0.719
$C_4I_4^{2+}$	1.8	1.451



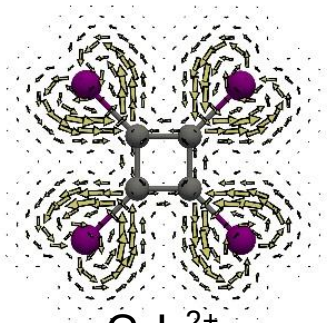
C_4I_4 – blue line

$C_4I_4^{2+}$ - orange line

*Per*iodo-cyclobutadiene – σ bond current strengths profile

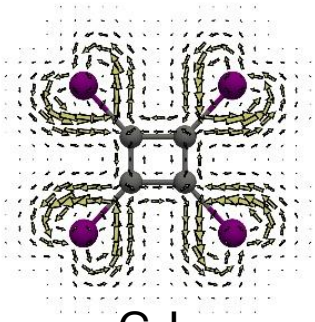


C_4I_4

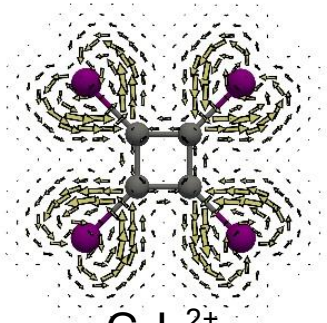


$C_4I_4^{2+}$

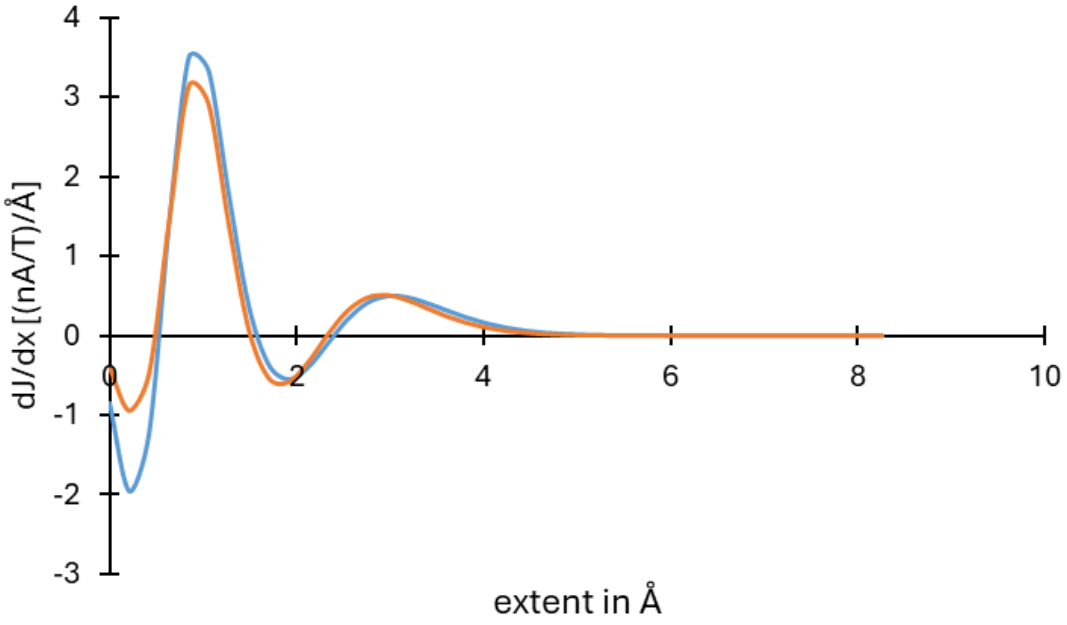
*Per*iodo-cyclobutadiene – σ bond current strengths profile



C_4I_4



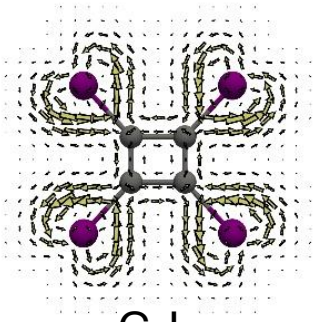
$C_4I_4^{2+}$



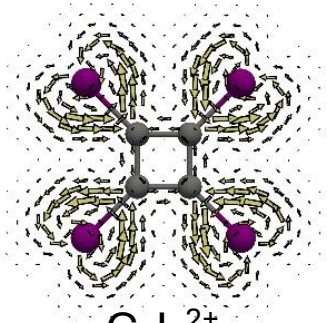
C_4I_4 – blue line

$C_4I_4^{2+}$ - orange line

*Per*iodo-cyclobutadiene – σ bond current strengths profile

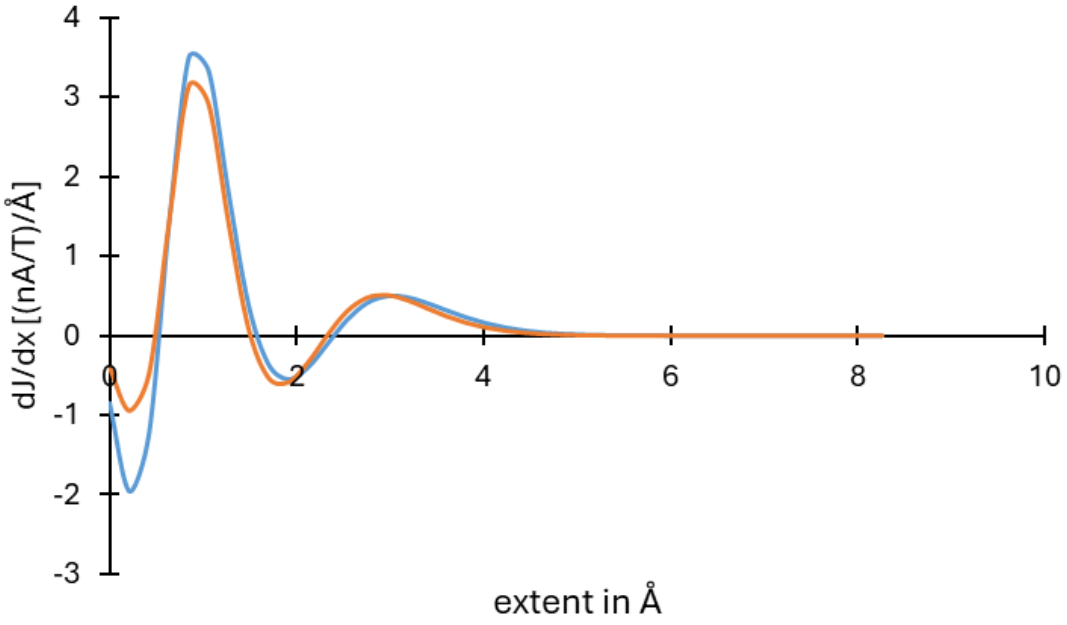


C_4I_4



$C_4I_4^{2+}$

	J^{σ} [nA T^{-1}]	$EDDB_{\sigma}$
C_4I_4	0.5	0.558
$C_4I_4^{2+}$	0.5	0.698



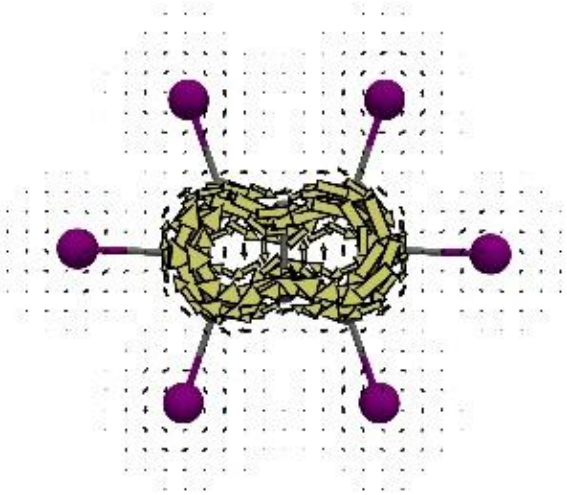
C_4I_4 – blue line

$C_4I_4^{2+}$ - orange line

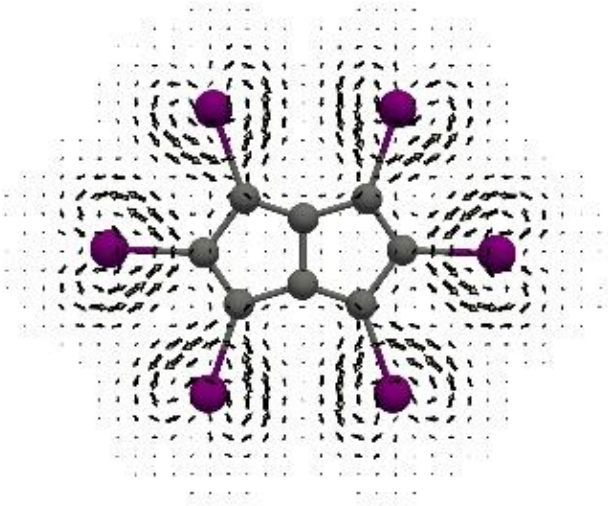
*Per*iodo-pentalene

C_8I_6

π-currents



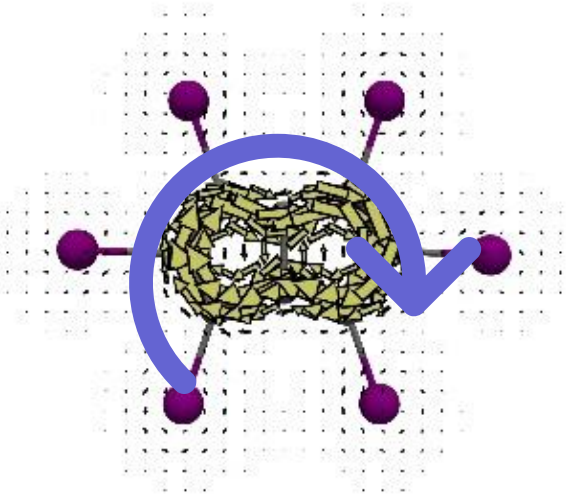
σ-currents



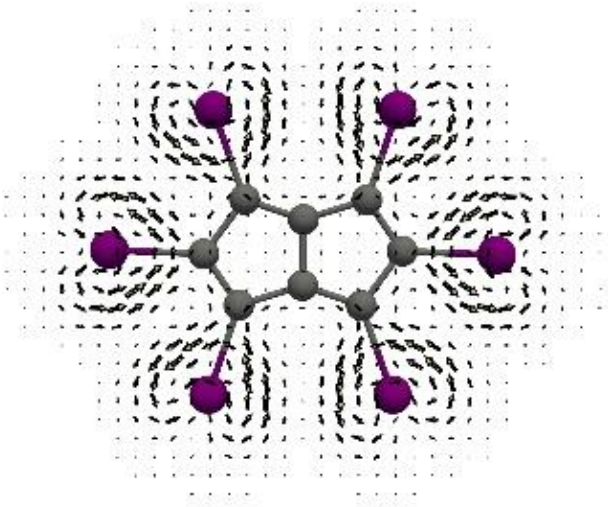
*Per*iodo-pentalene

C_8I_6

π-currents



σ-currents

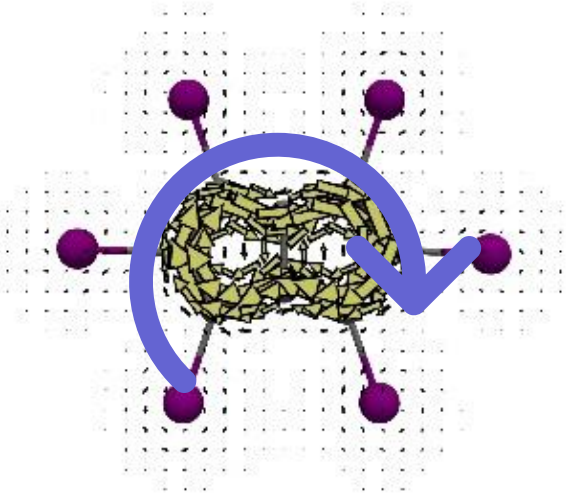


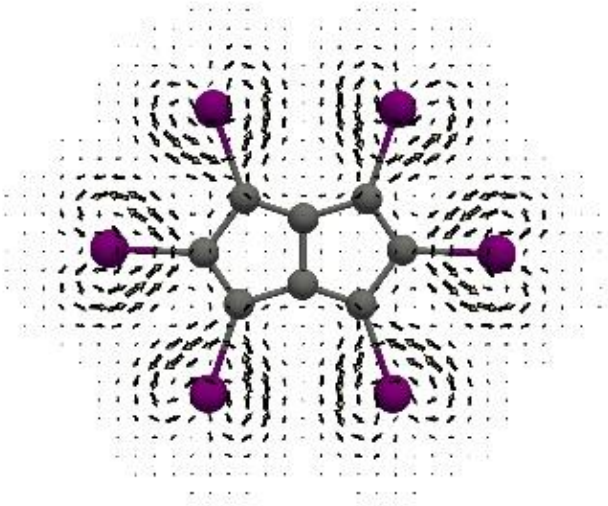
*Per*iodo-pentalene

π-currents

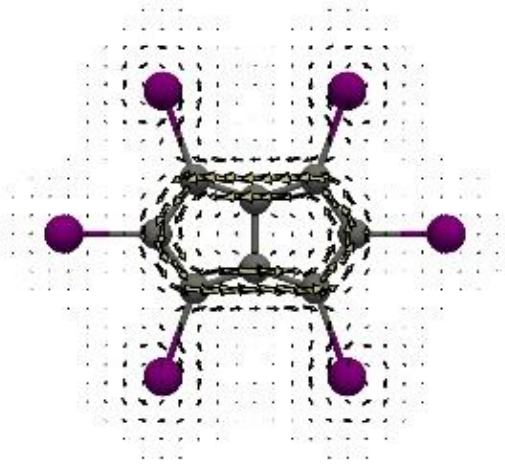
σ-currents

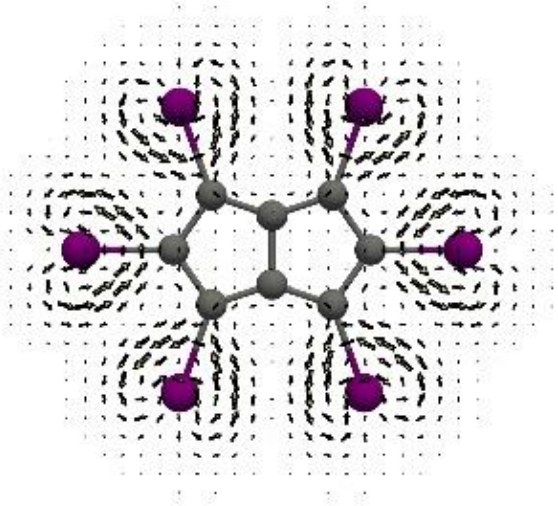
C_8I_6





$C_8I_6^{2+}$



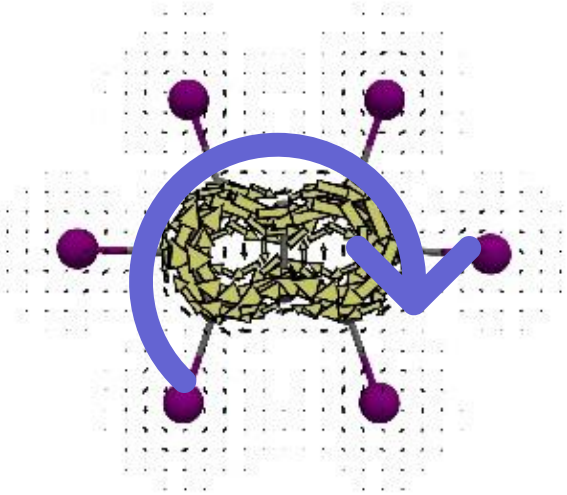


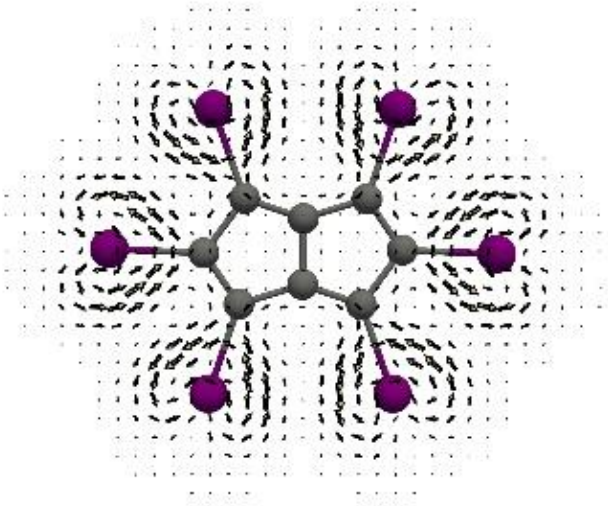
*Per*iodo-pentalene

π-currents

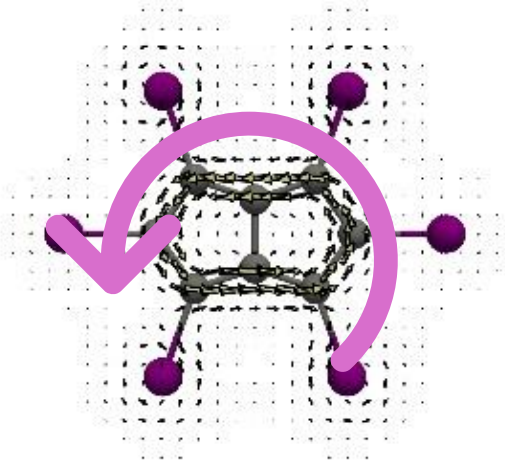
σ-currents

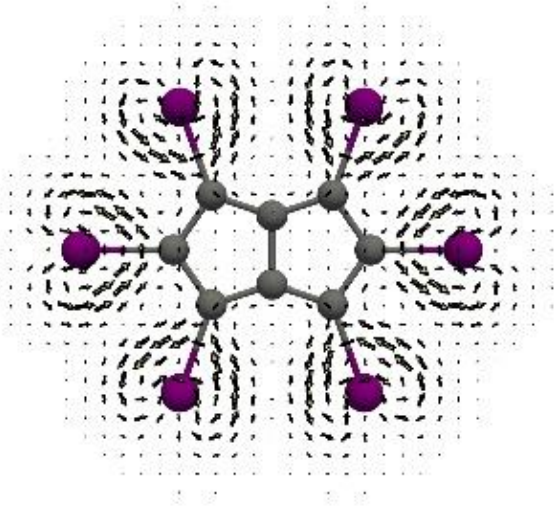
C_8I_6





$C_8I_6^{2+}$



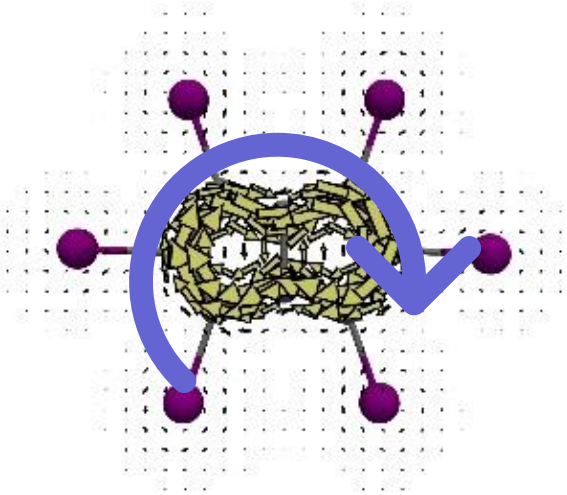


*Per*iodo-pentalene

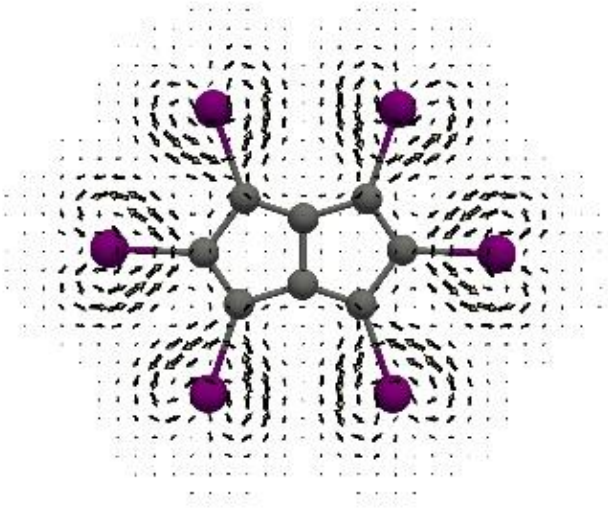
π-currents

σ-currents

C_8I_6

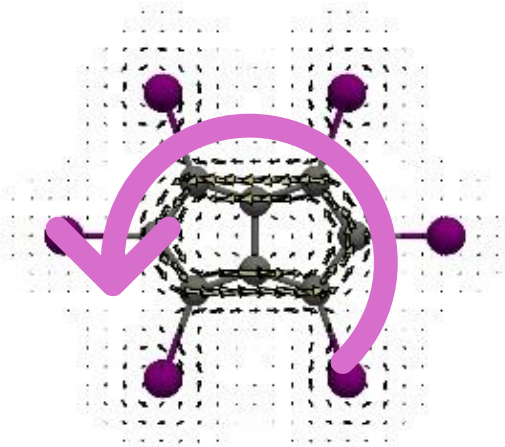


8 electrons

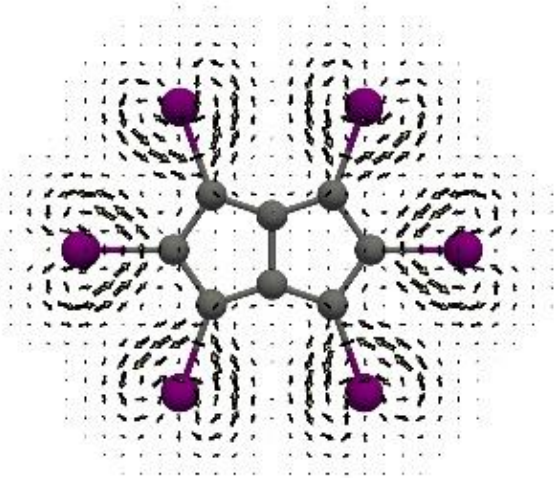


12 electrons

$C_8I_6^{2+}$

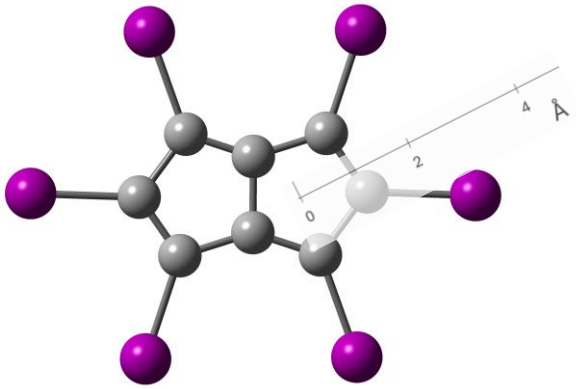


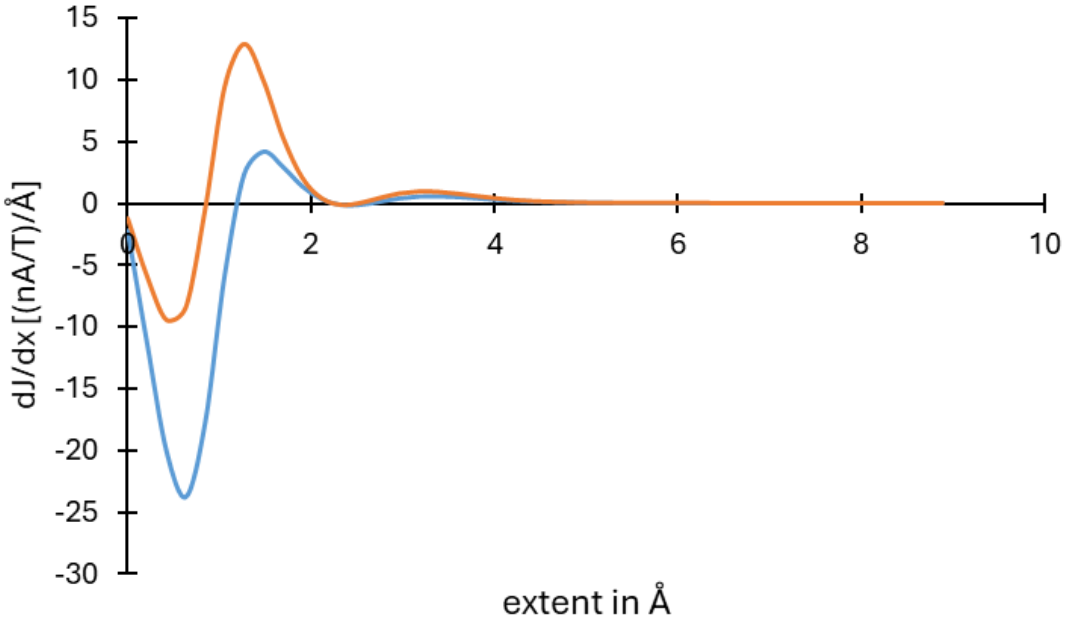
6 electrons



12 electrons

*Per*iodo-pentalene – bond current strengths profile

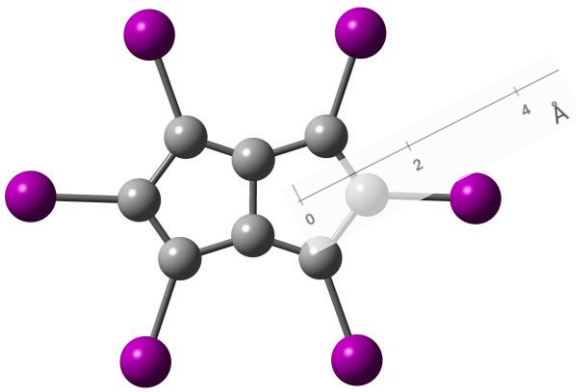




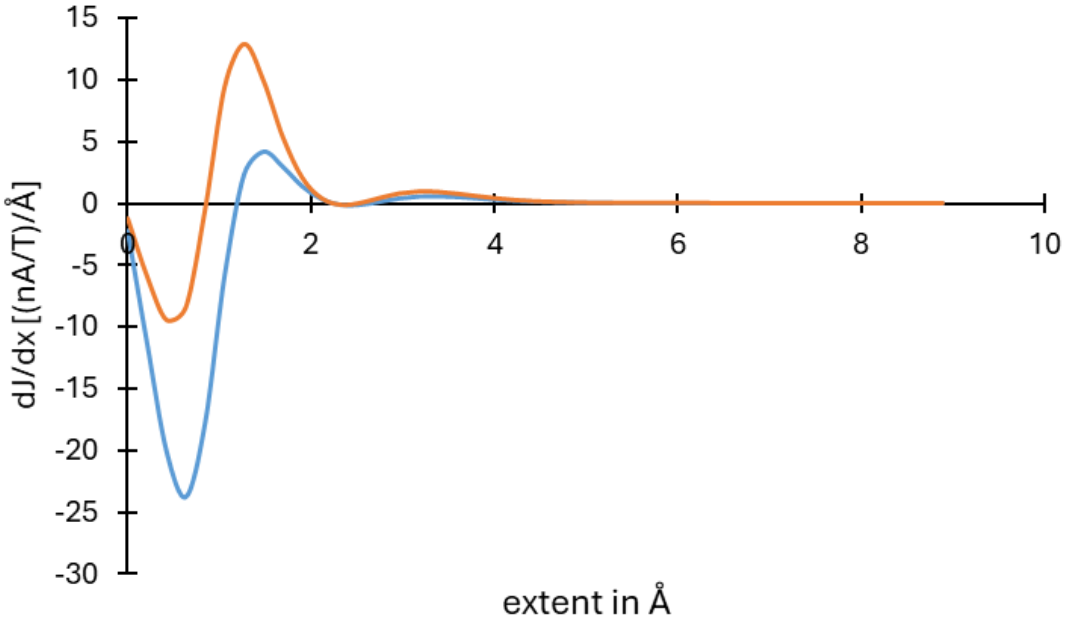
C_8I_6 – blue line

$C_8I_6^{2+}$ - orange line

*Per*iodo-pentalene – bond current strengths profile



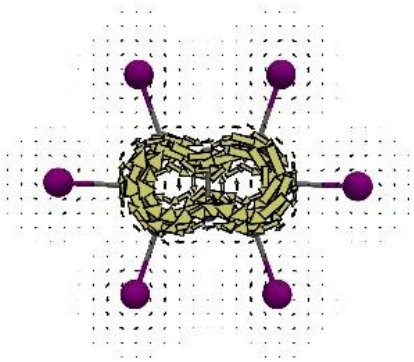
		J [nA T^{-1}]	EDDB	I_{ring}
C_8I_6	C_8	-14.8	2.511	0.516
	I_6	0.5	0.214	0.051
$C_8I_6^{2+}$	C_8	3.1	4.481	0.548
	I_6	1.0	0.530	0.043



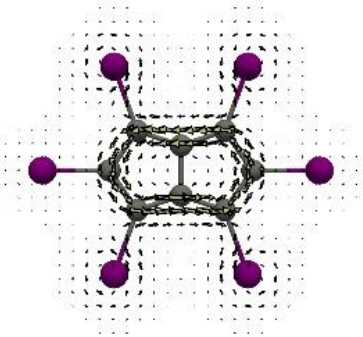
C_8I_6 – blue line

$C_8I_6^{2+}$ - orange line

*Per*iodo-pentalene – π bond current strengths profile

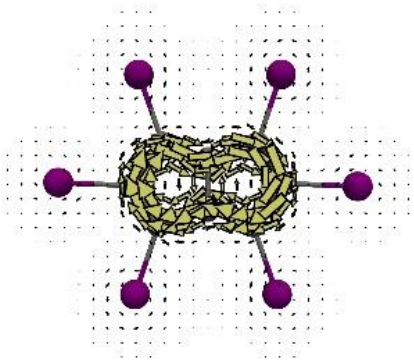


C_8I_6

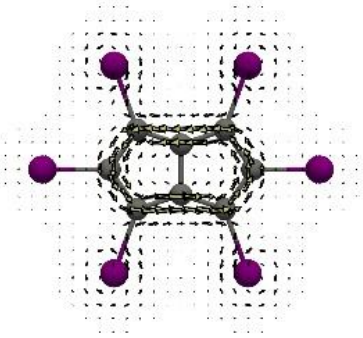


$C_8I_6^{2+}$

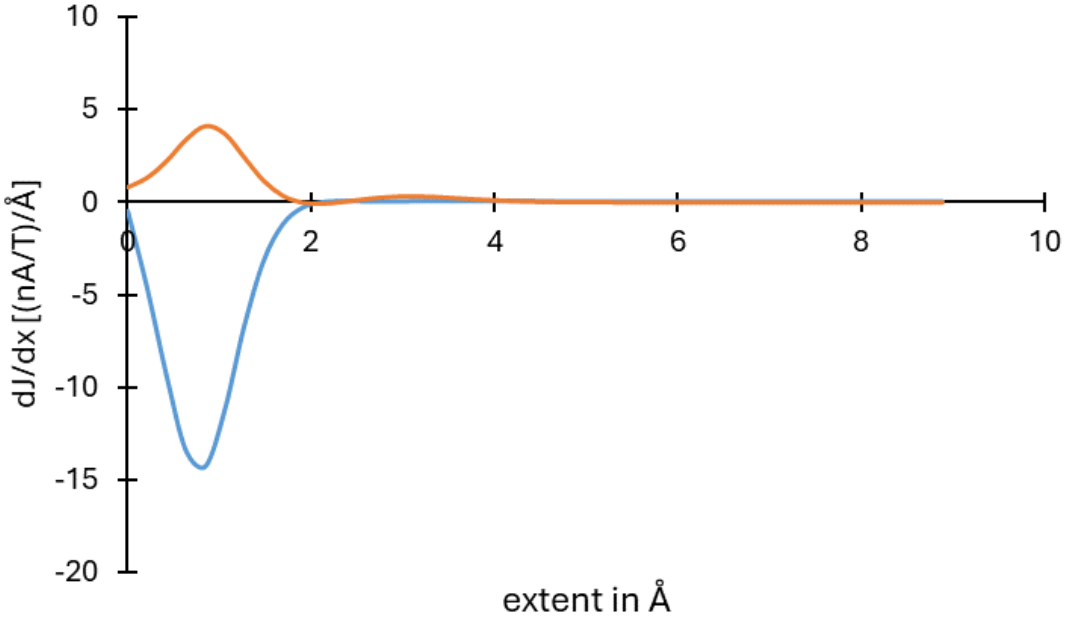
*Per*iodo-pentalene – π bond current strengths profile



C_8I_6



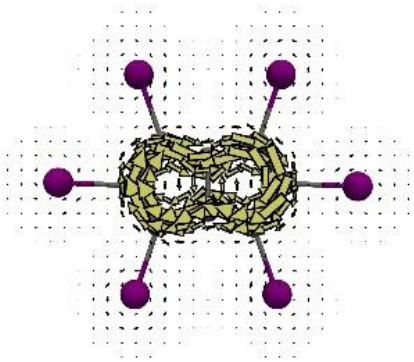
$C_8I_6^{2+}$



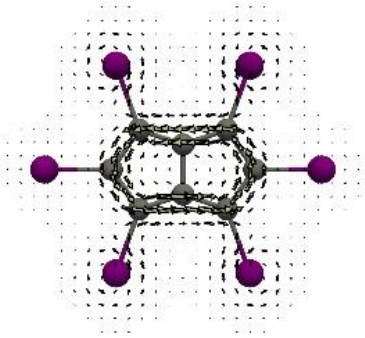
C_8I_6 – blue line

$C_8I_6^{2+}$ - orange line

*Per*iodo-pentalene – π bond current strengths profile

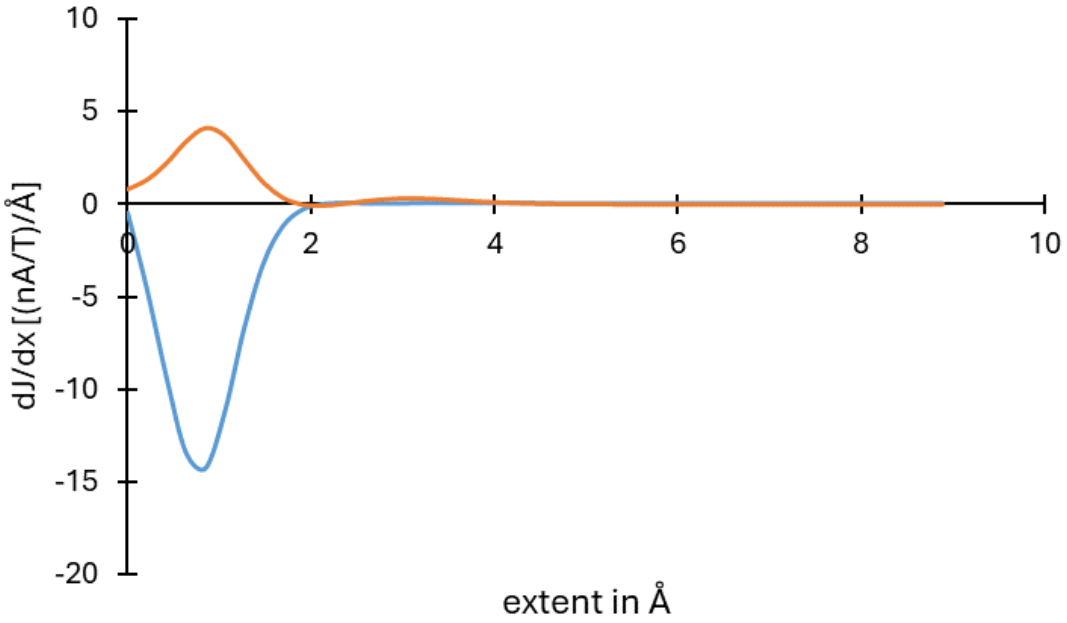


C_8I_6



$C_8I_6^{2+}$

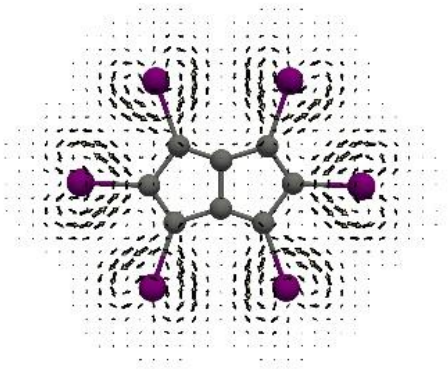
	J^{π} [nA T^{-1}]	$EDDB_{\pi}$
C_8I_6	-13.8	3.297
$C_8I_6^{2+}$	4.1	5.340



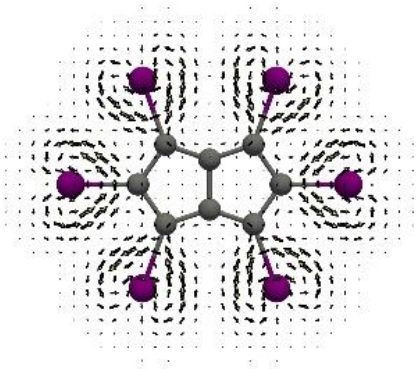
C_8I_6 – blue line

$C_8I_6^{2+}$ - orange line

*Per*iodo-pentalene – σ bond current strengths profile

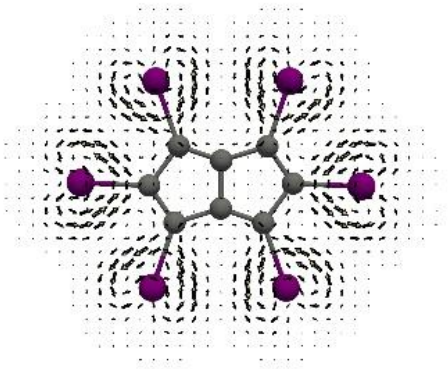


C_8I_6

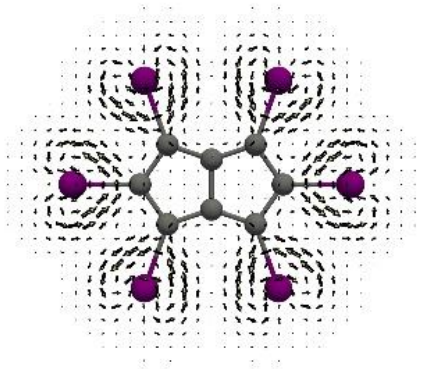


$C_8I_6^{2+}$

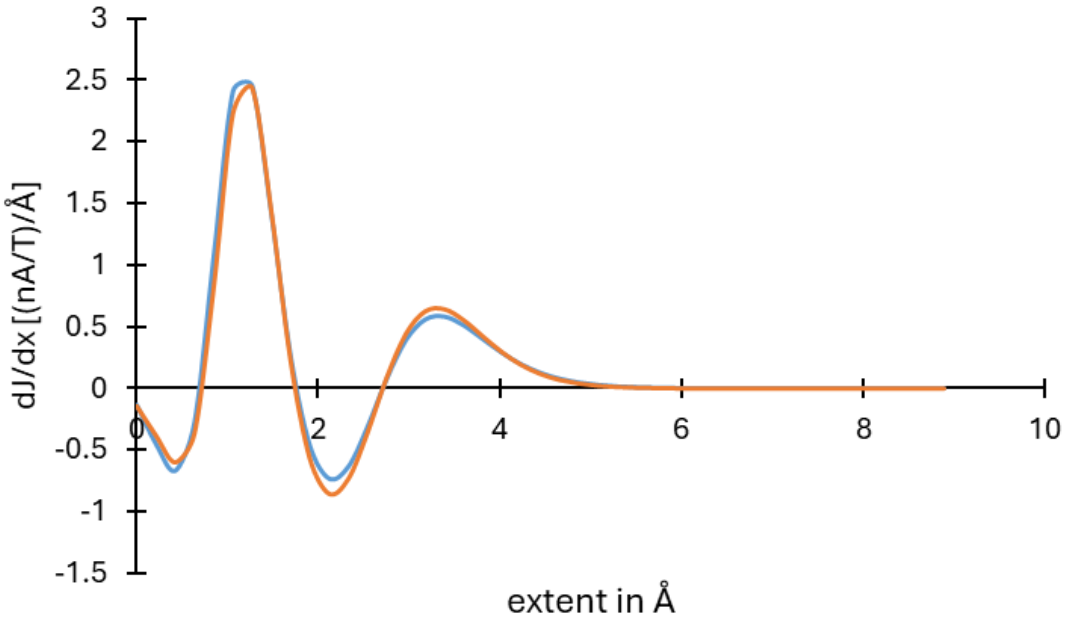
*Per*iodo-pentalene – σ bond current strengths profile



C_8I_6



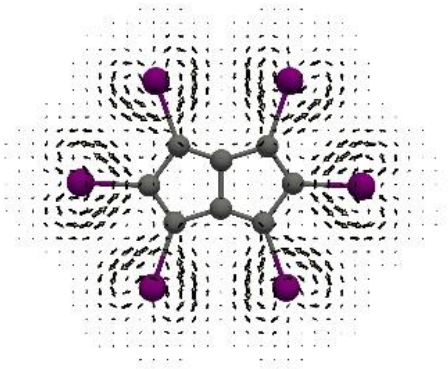
$C_8I_6^{2+}$



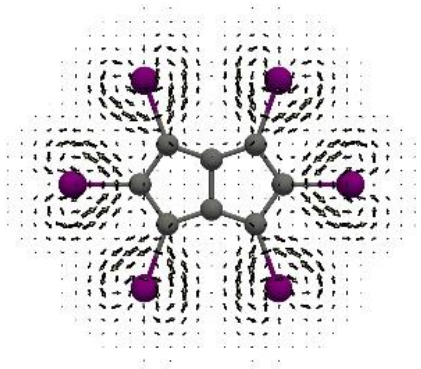
C_8I_6 – blue line

$C_8I_6^{2+}$ - orange line

*Per*iodo-pentalene – σ bond current strengths profile

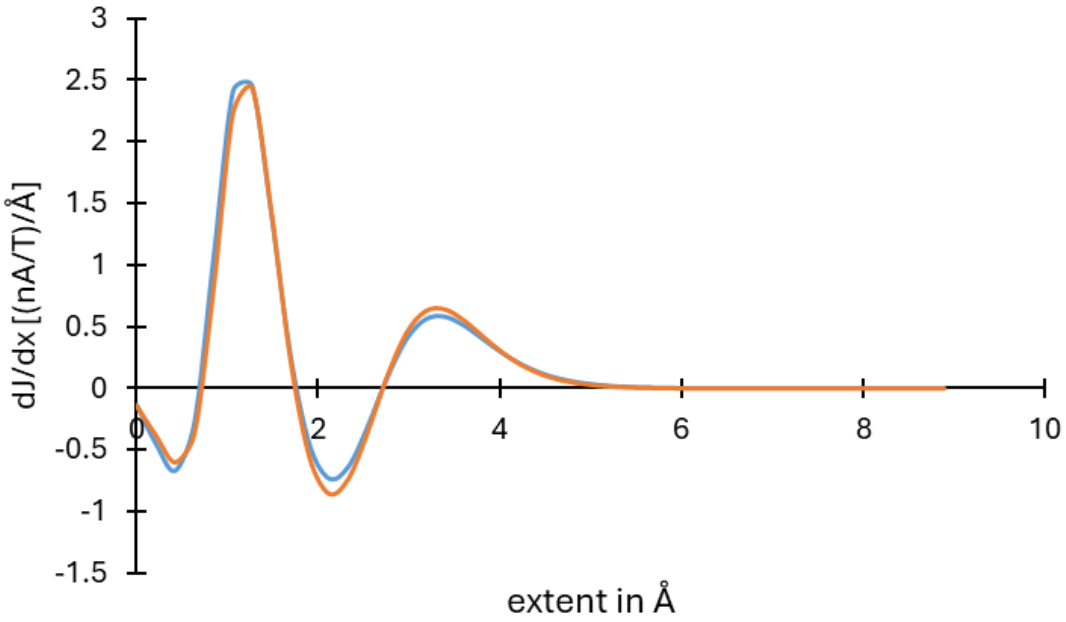


C_8I_6



$C_8I_6^{2+}$

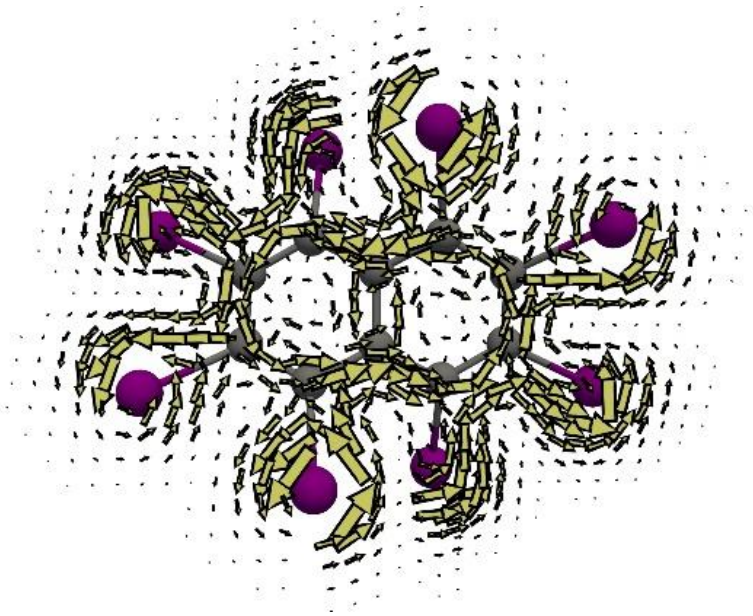
	J^{σ} [nA T^{-1}]	$EDDB_{\sigma}$
C_8I_6	1.0	0.609
$C_8I_6^{2+}$	0.9	0.885



C_8I_6 – blue line

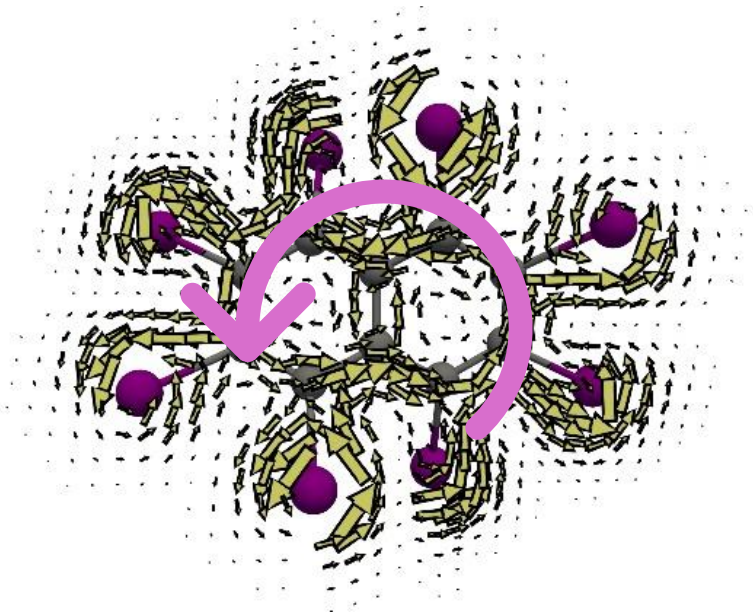
$C_8I_6^{2+}$ - orange line

*Per*iodo-naphtalene



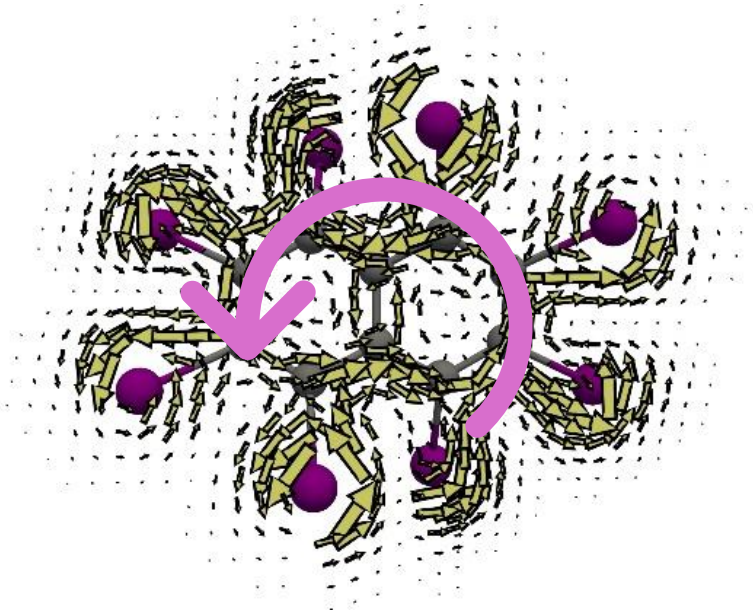
$C_{10}I_8$

*Per*iodo-naphtalene

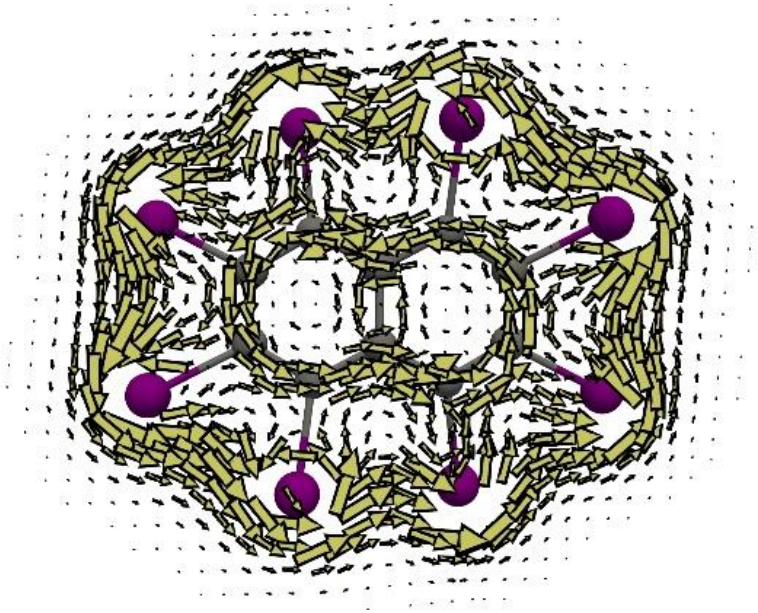


$C_{10}I_8$

*Per*iodo-naphtalene

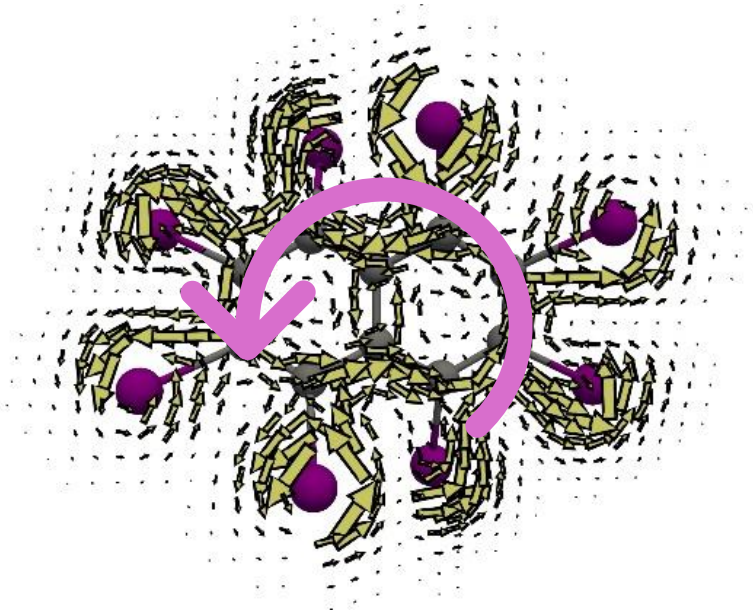


$C_{10}I_8$

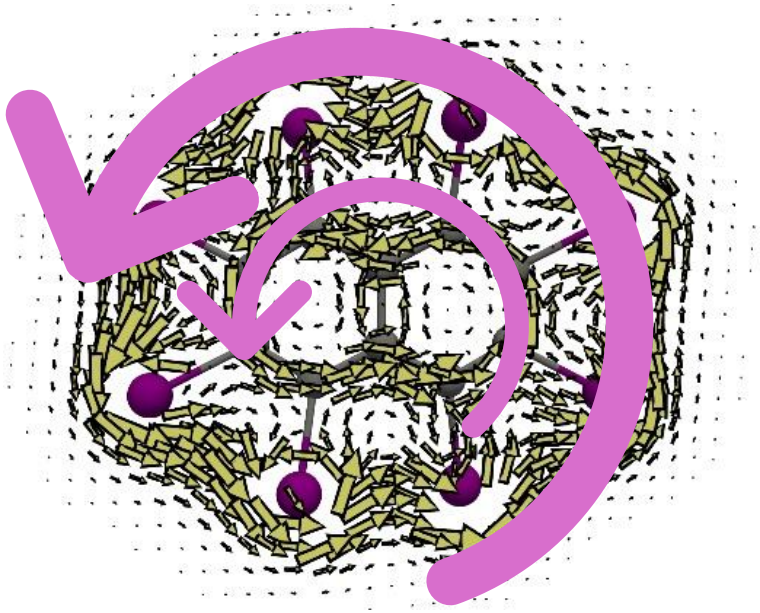


$C_{10}I_8^{2+}$

*Per*iodo-naphtalene

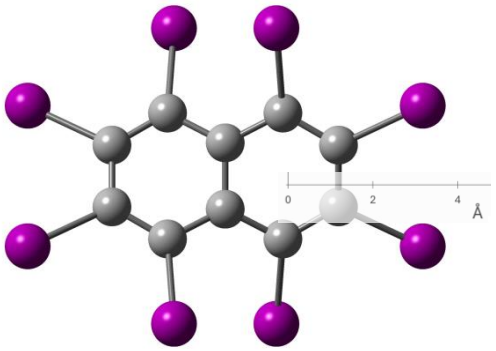


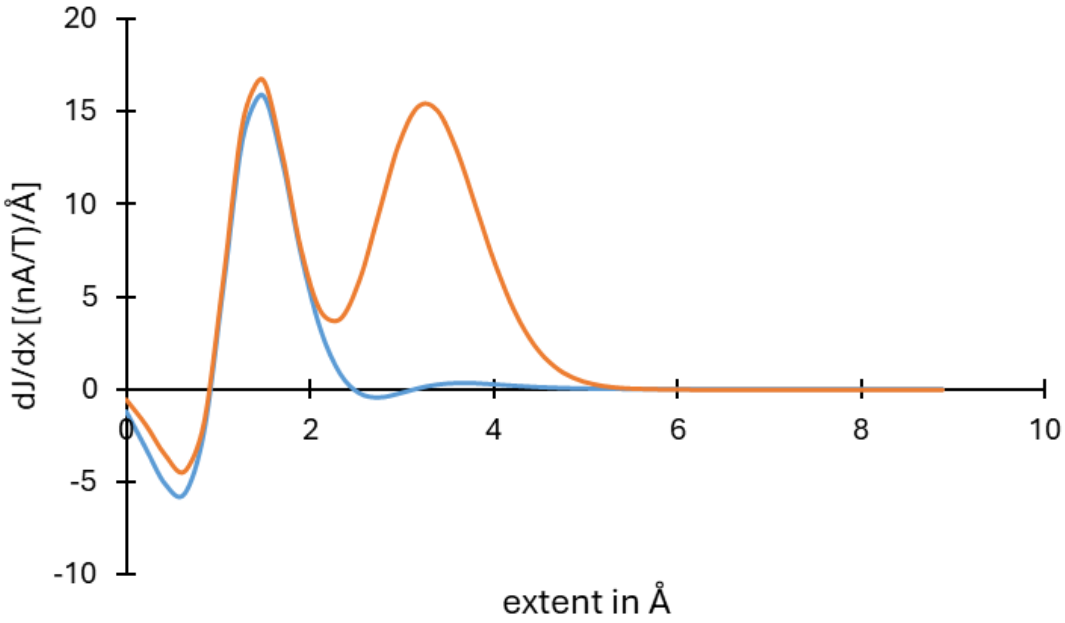
$C_{10}I_8$



$C_{10}I_8^{2+}$

*Per*iodo-naphtalene – bond current strengths profile

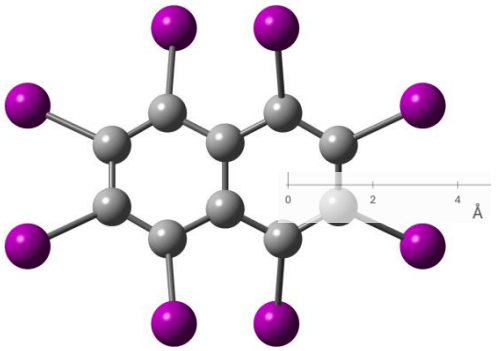




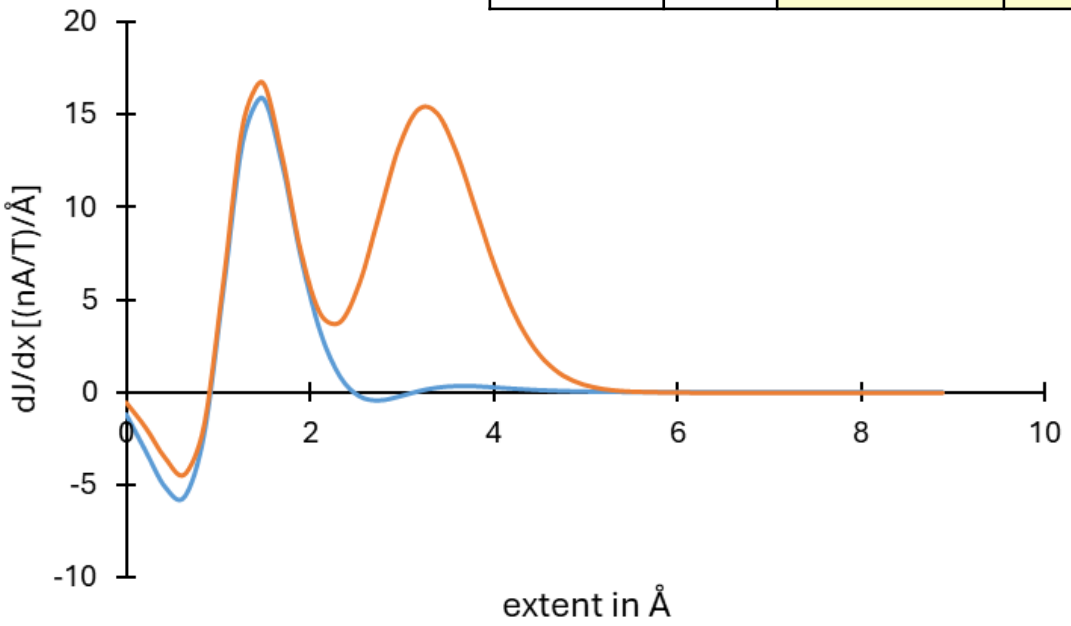
$C_{10}I_8$ – blue line

$C_{10}I_8^{2+}$ - orange line

*Per*iodo-naphtalene – bond current strengths profile



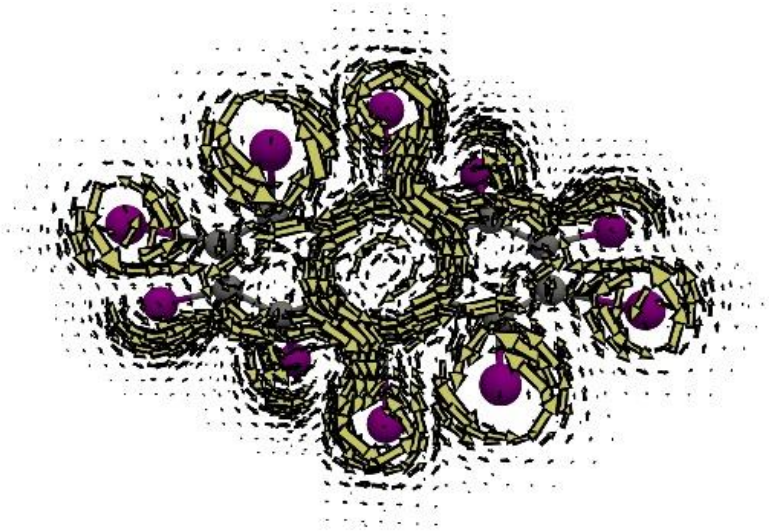
		J [nA T^{-1}]	EDDB	I_{ring}
$C_{10}I_8$	C_{10}	8.6	5.918	0.573
	I_8	0.3	0.252	0.080
$C_{10}I_8^{2+}$	C_{10}	10.5	7.085	0.590
	I_8	21.4	5.825	0.165



$C_{10}I_8$ – blue line

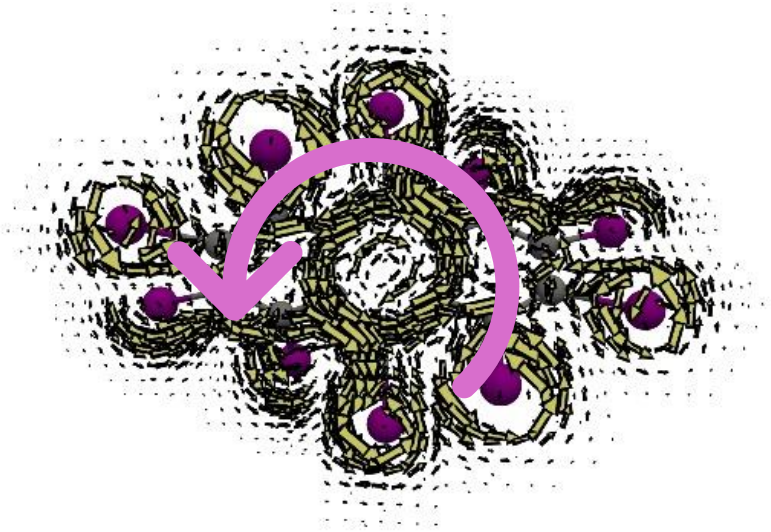
$C_{10}I_8^{2+}$ - orange line

*Per*iodo-anthracene



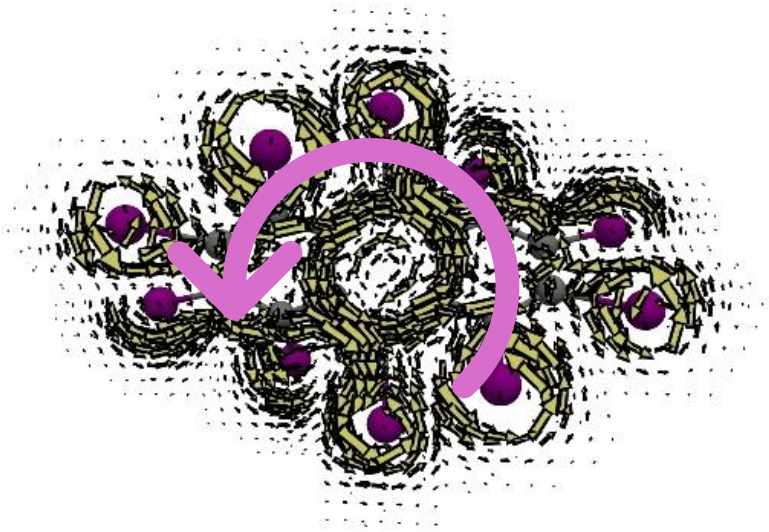
$C_{14}I_{10}$

*Per*iodo-anthracene

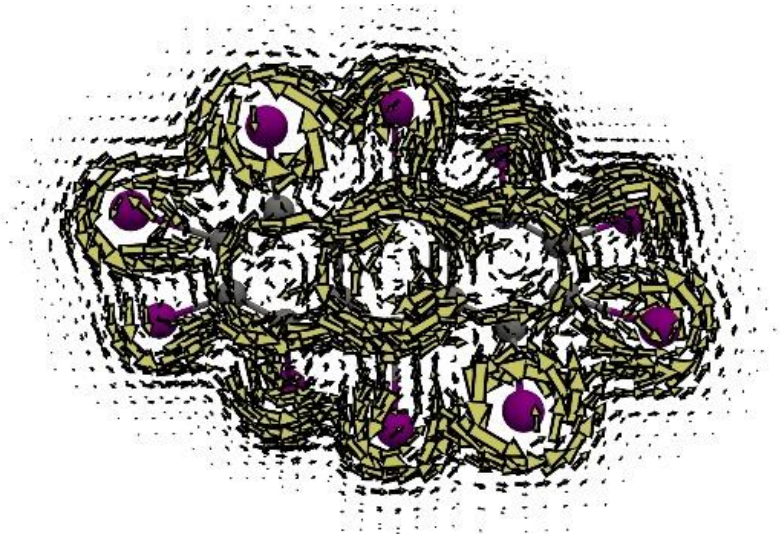


$C_{14}I_{10}$

*Per*iodo-anthracene

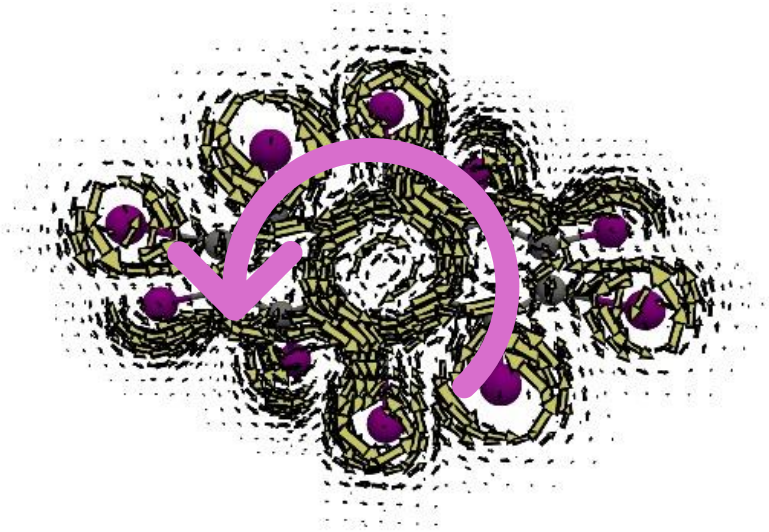


$C_{14}I_{10}$



$C_{14}I_{10}^{2+}$

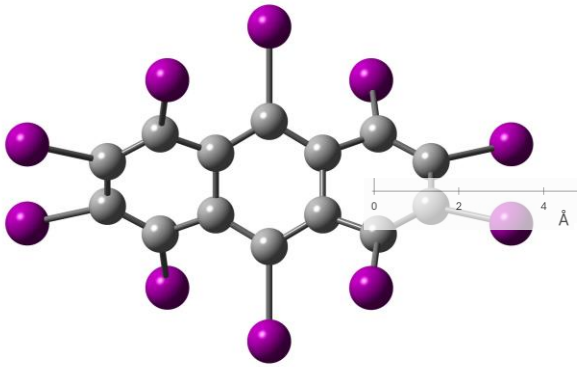
*Per*iodo-anthracene

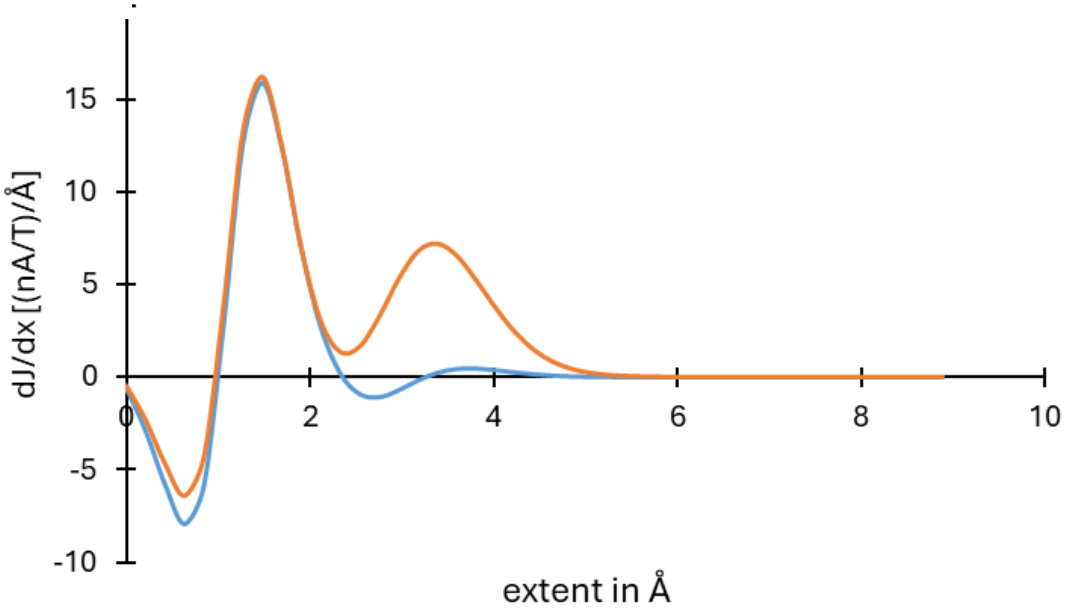


$C_{14}I_{10}$

$C_{14}I_{10}^{2+}$

*Per*iodo-anthracene – bond current strengths profile

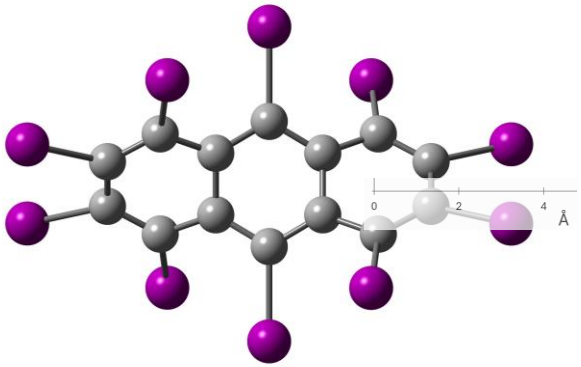




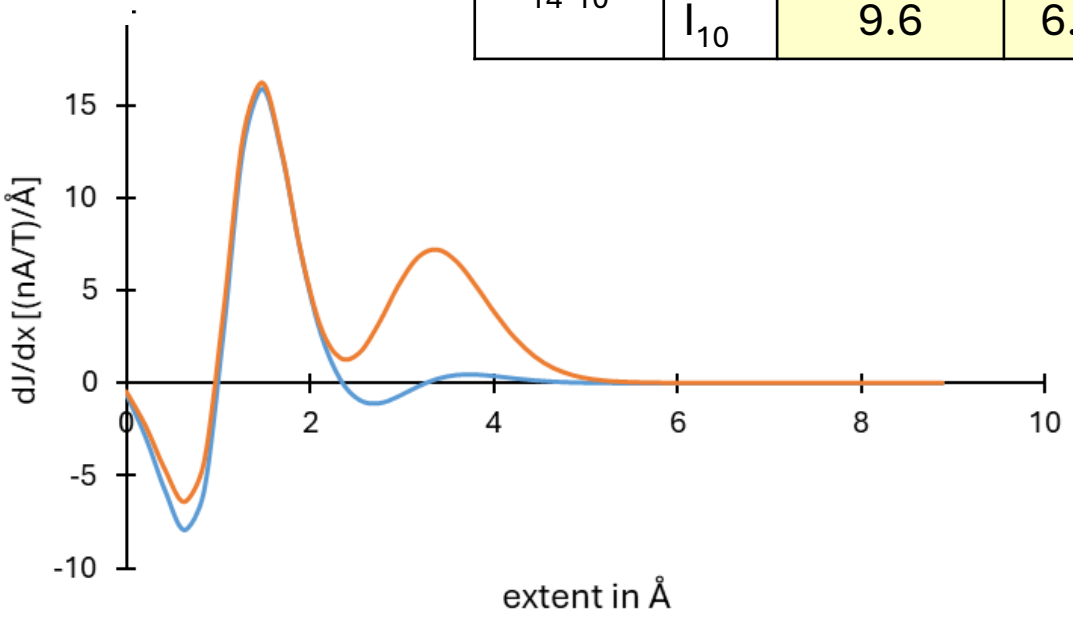
$C_{14}I_{10}$ – blue line

$C_{14}I_{10}^{2+}$ - orange line

*Peri*odo-anthracene – bond current strengths profile



		J [nA T^{-1}]	EDDB	I_{ring}
$C_{14}I_{10}$	C_{14}	6.4	8.130	0.556
	I_{10}	-0.2	0.301	0.066
$C_{14}I_{10}^{2+}$	C_{14}	8.3	8.916	0.570
	I_{10}	9.6	6.089	0.165



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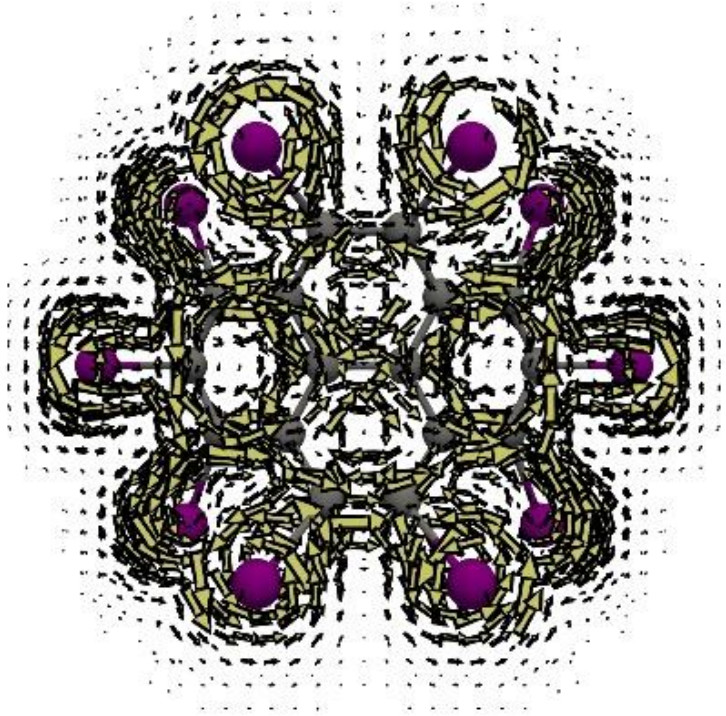
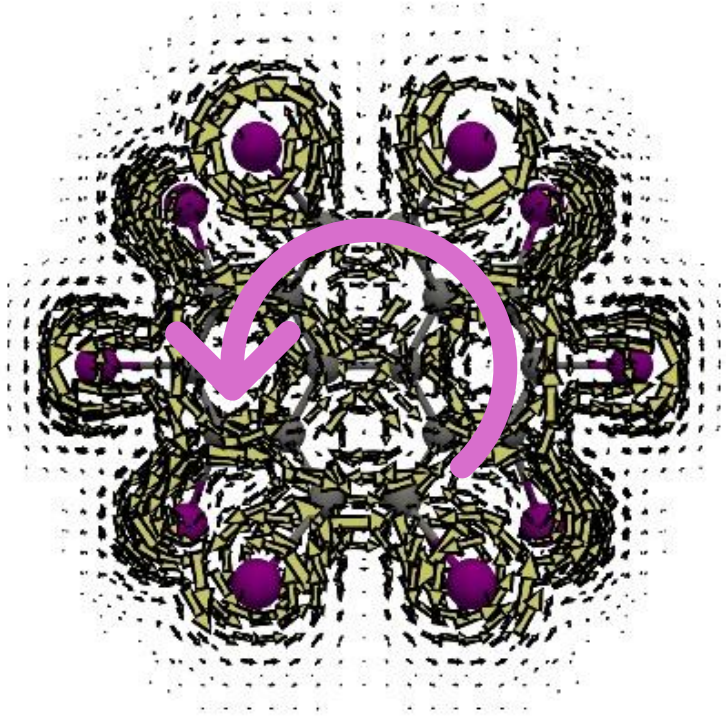
*Per*iodo-perylene



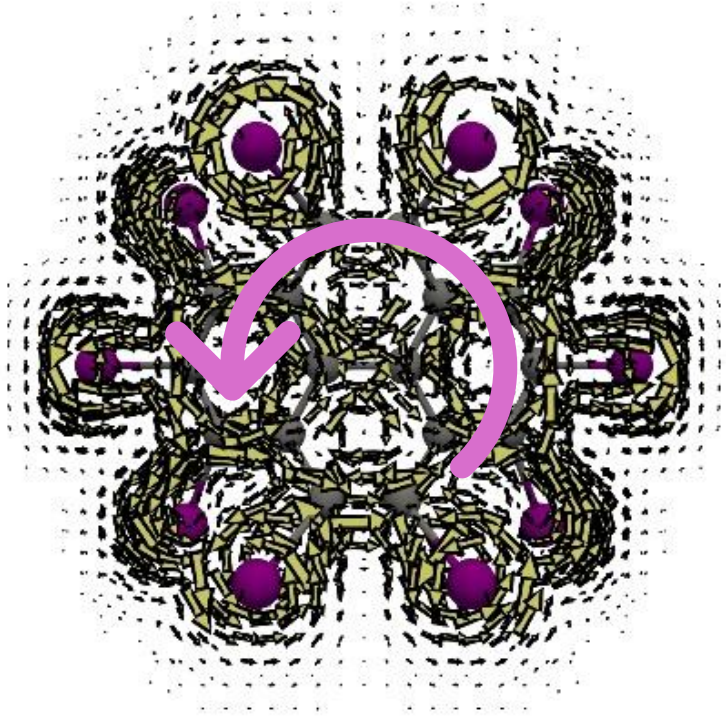
$C_{16}I_{10}$

*Per*iodo-perylene

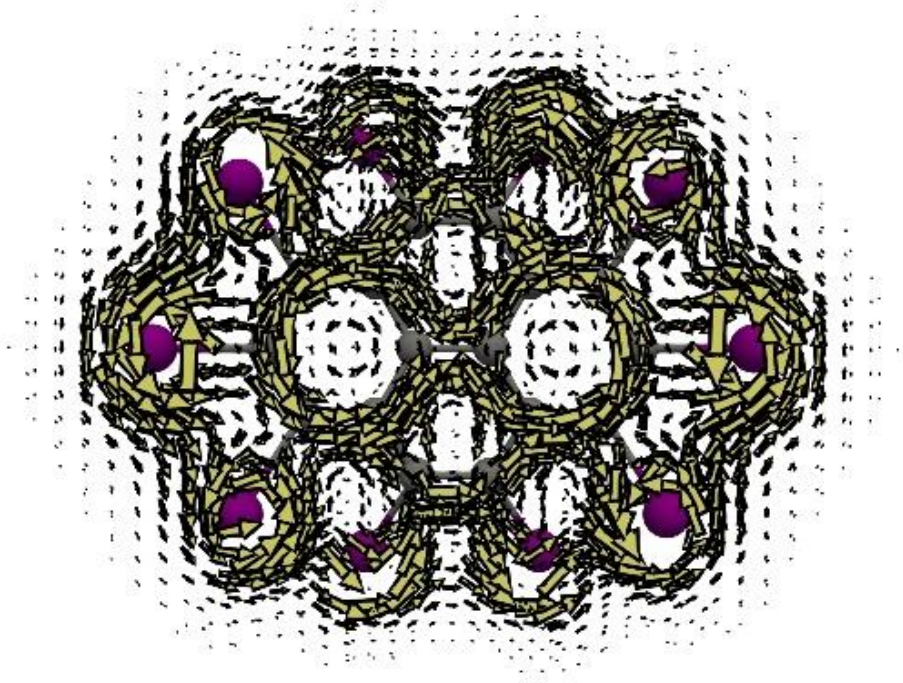


$C_{16}I_{10}$

*Per*iodo-perylene

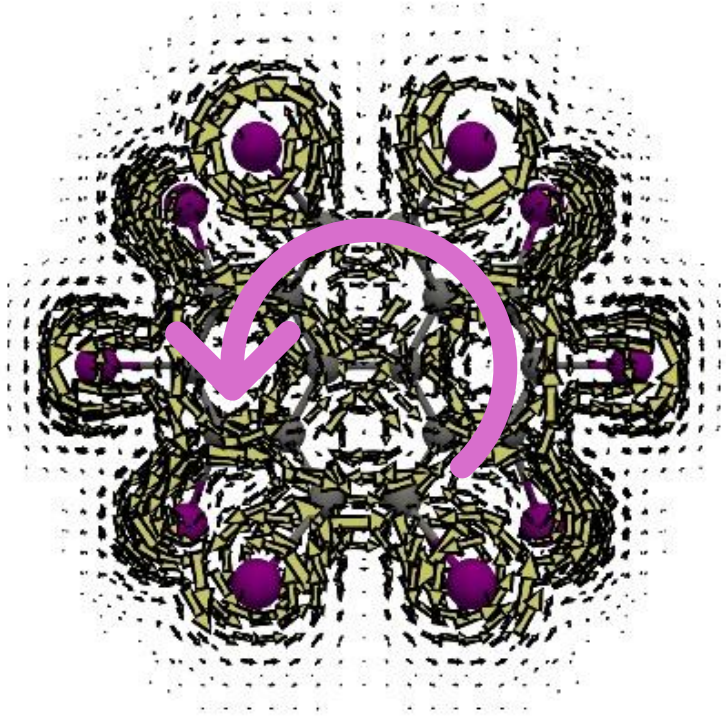


$C_{16}I_{10}$

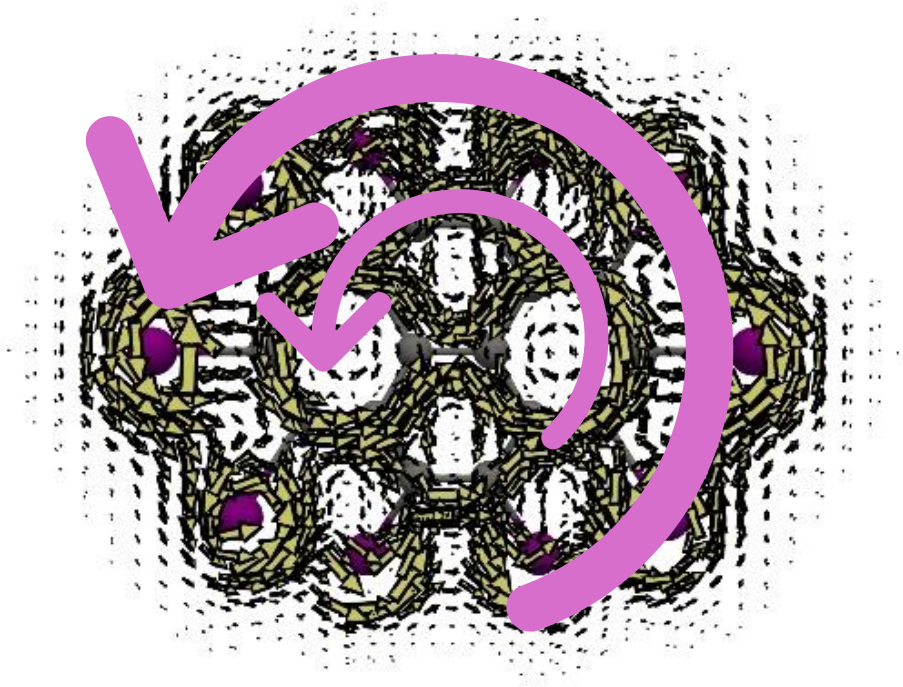


$C_{16}I_{10}^{2+}$

*Per*iodo-perylene

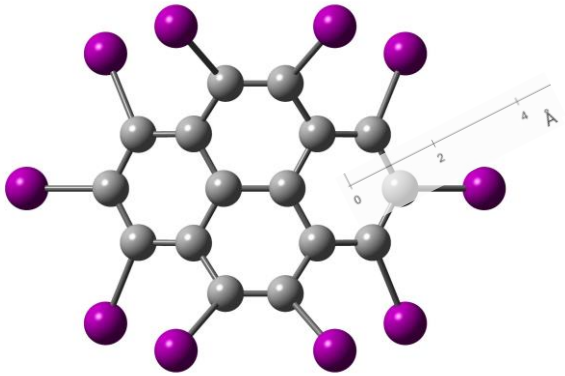


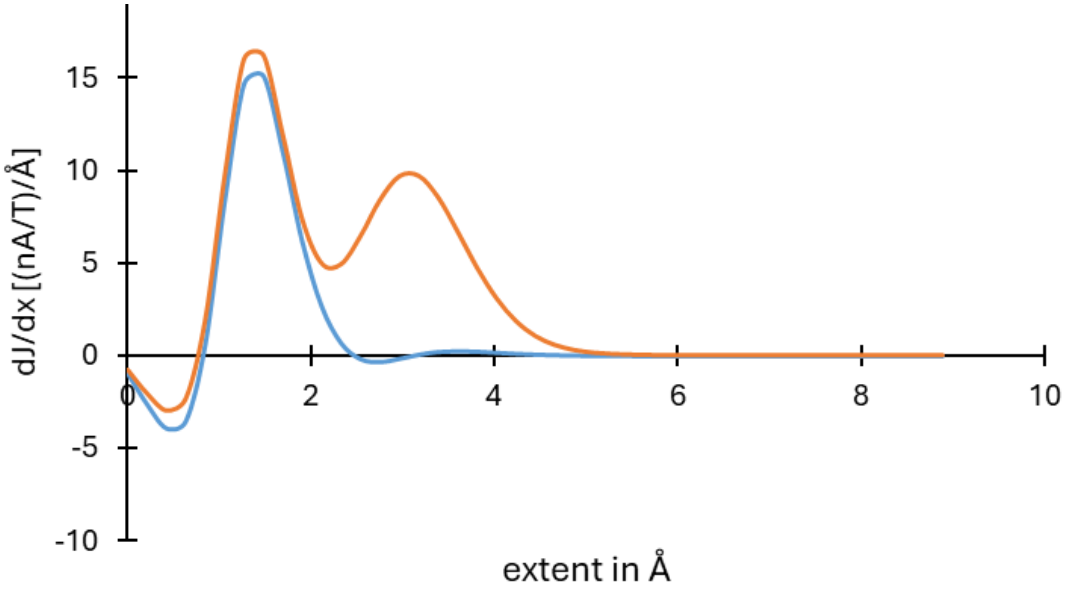
$C_{16}I_{10}$



$C_{16}I_{10}^{2+}$

*Per*iodo-perylene – bond current strengths profile





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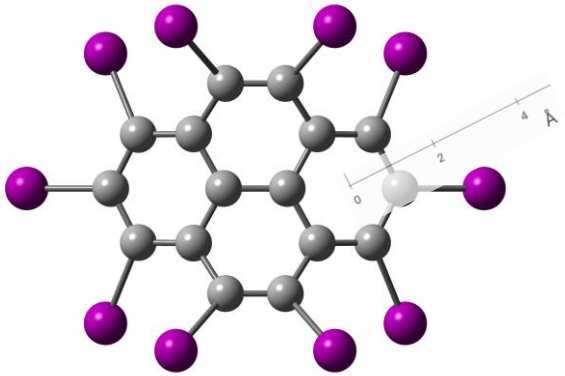
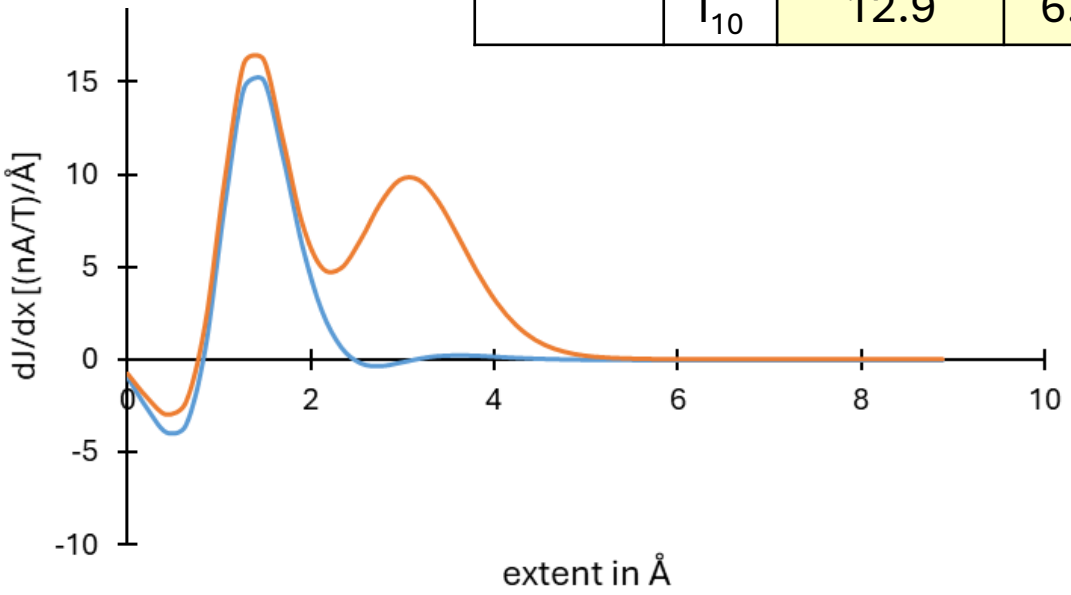


		J [nA T^{-1}]	EDDB	I_{ring}
$C_{16}I_{10}$	C_{16}	10.2	7.233	0.542
	I_{10}	0.1	0.266	0.087
$C_{16}I_{10}^{2+}$	C_{16}	13.7	7.656	0.560
	I_{10}	12.9	6.146	0.172



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Conclusions

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- Our results indicate that *per*iodo-naphtalene dication, *per*iodo-anthracene dication and *per*iodo-perylene dication are **double aromatic** systems.
- On the other side, *per*iodo-pentalene dication is π-aromatic system.