MAGIC 2024

An Exploration of Systems with Double 2D- and 3D-aromaticity

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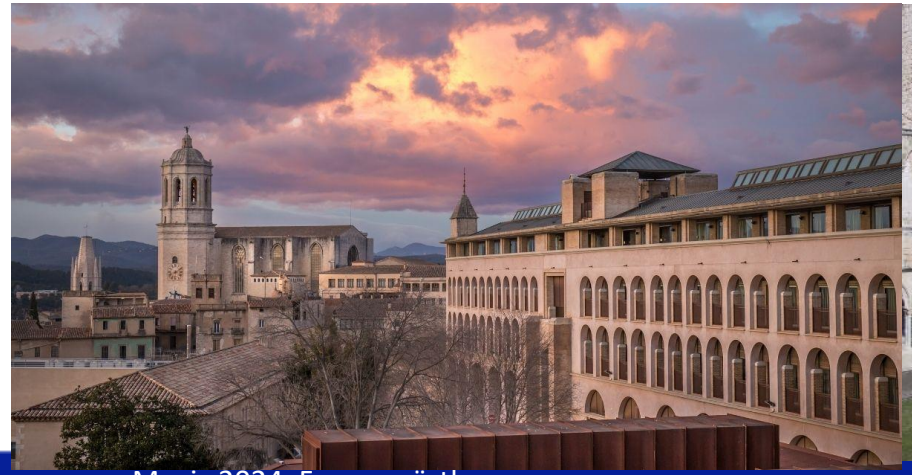
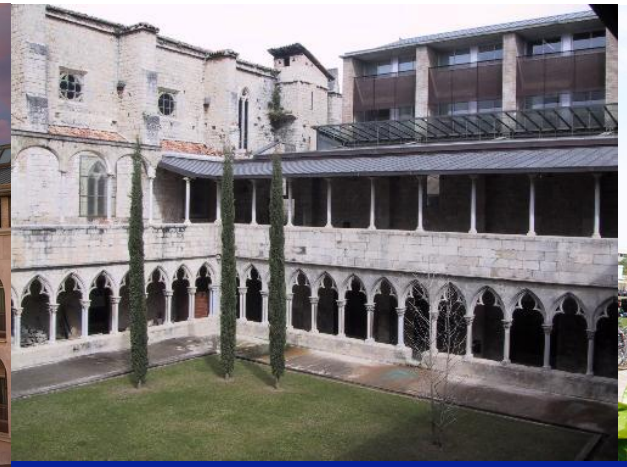
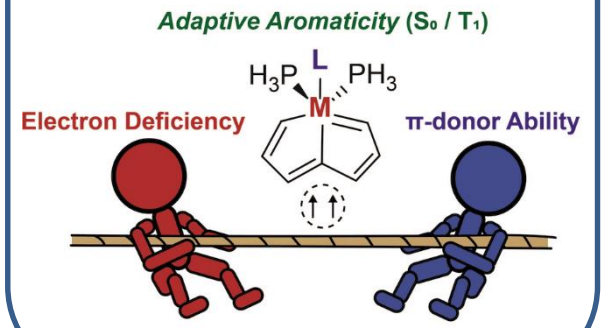




Universitat de Girona

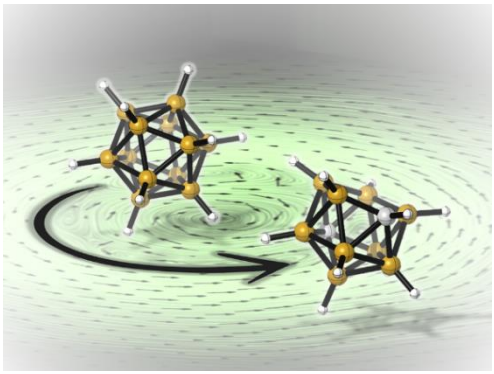
iQCC

Excited state aromaticity

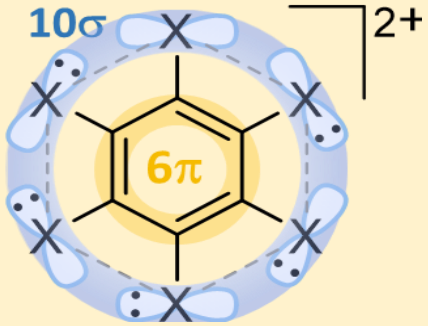


Macrocyclic aromaticity

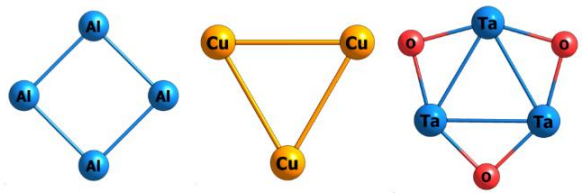
3D-aromaticity



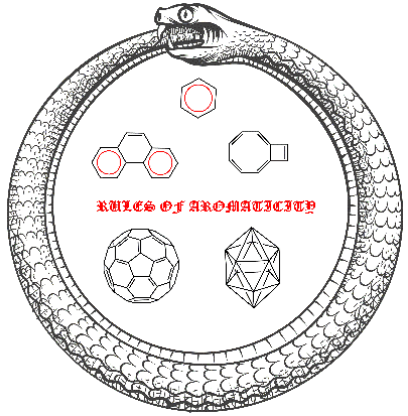
Double aromaticity



Metalla-aromaticity



Aromaticity rules

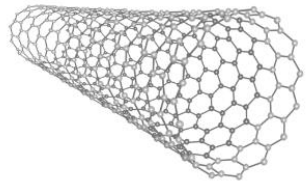


Universitat de Gir

Dr. Sílvia Escayola, PhD thesis

RC → history

Faraday discovered benzene **1825**



discovery of nanotubes **1991**

discovery of fullerenes **1985**

Hirsch $2(N+1)^2$ rule **2000**

all-metal aromaticity **2001**

synthesis of porphyrin nanoring and δ-aromaticity **2007**

all-metal fullerene $[K@Au_{12}Sb_{20}]^{5-}$ **2023**

metallabenzenes **1982**

Möbius aromaticity **1964**

3D aromaticity **1962**

conflicting aromaticity **2003**

φ-aromaticity **2008**

2005

1990

1980

1950

1825

Hofmann introduces the term aromaticity **1856**

synthesis of pyridine **1868**

1911 COT

1834 Mitscherlich determined benzene formula: C_6H_6

1865 benzene structure Kekulé

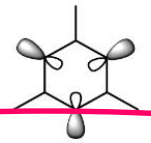
1931 Hückel 4n+2 rule

1938 aromatic transition states

1965 Woodward–Hoffmann rules

1972 Baird 4n rule

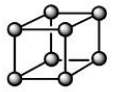
Clar π-sextets



1979 double aromaticity 3,5-dehydrophenyl cation

2005 d-orbital aromaticity

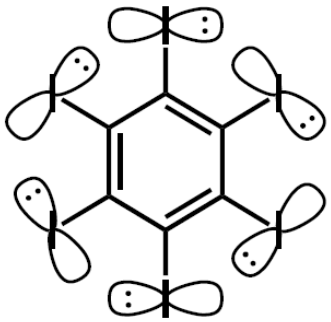
2015 cubic aromaticity



2019 isolation of cyclo[18]carbon

C_6I_6

Neutral

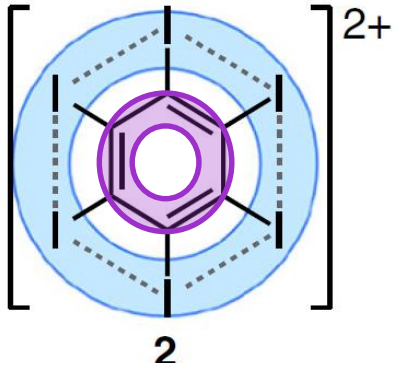


1

12 Electrons

2e⁻ oxidation

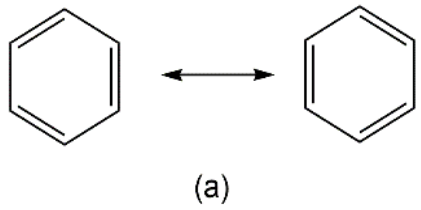
Dication



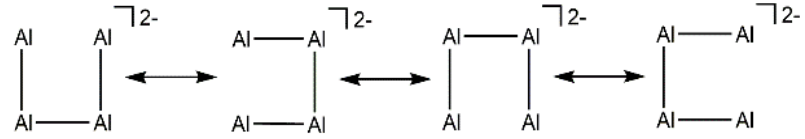
2

6π Hückel-aromatic

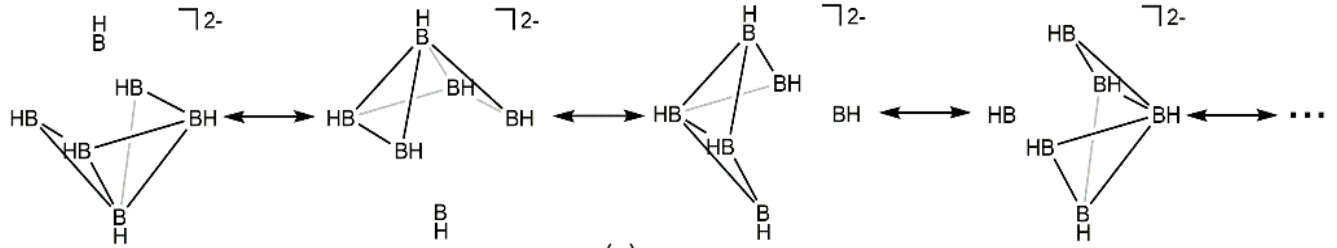
10σ Hückel-aromatic



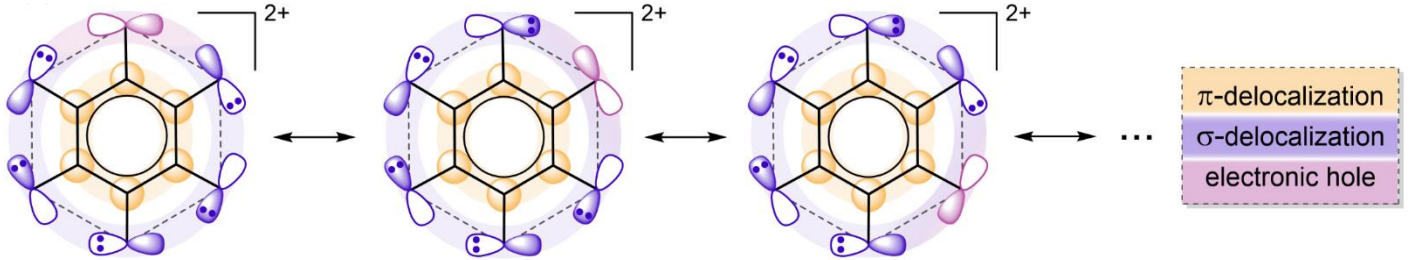
(a)



(b)



(c)

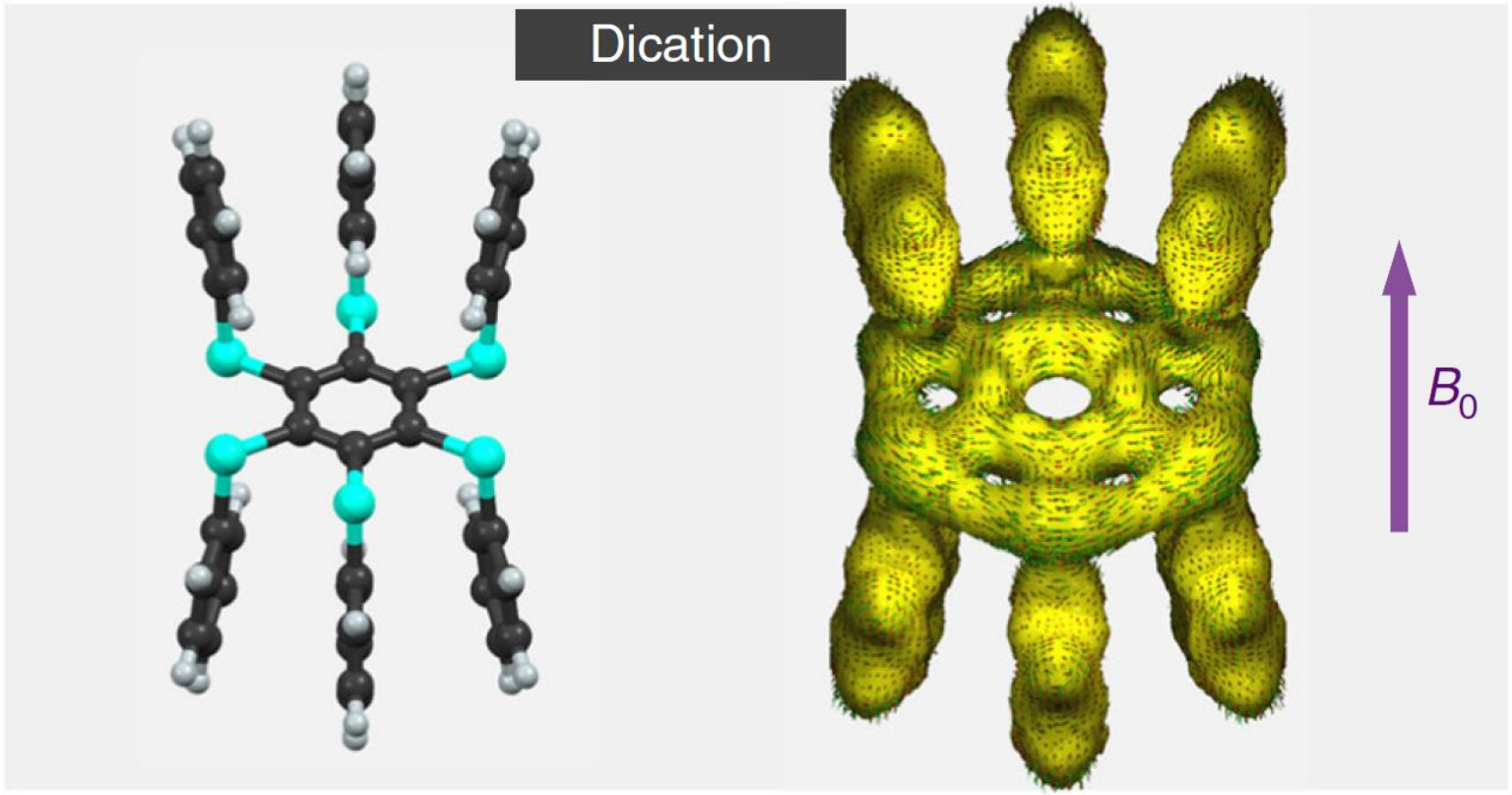


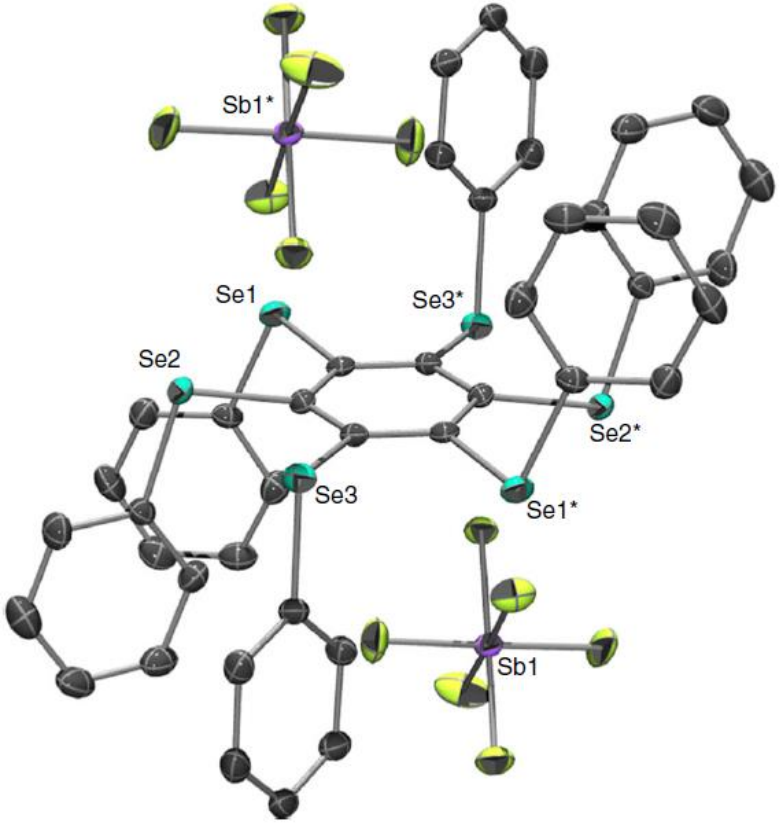
Double oxidation of C_6I_6 is required to open a hole in one of the 5*p* orbitals of iodine that generates six possible resonance structures ($C_6Cl_6^{+2}$ has a triplet ground state).

D. J. Sagl, J. C. Martin, *J. Am. Chem. Soc.* **1988**, *110*, 5827.

$C_6(SePh)_6^{2+}$

bond distances: C−C [1.382(7)–1.399(7) Å]
Se−Se [3.240(1)–3.338(1) Å]



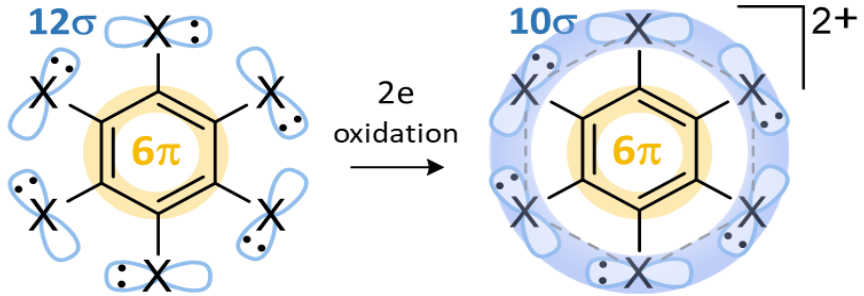


dication of hexakis(phenylselenyl)benzene

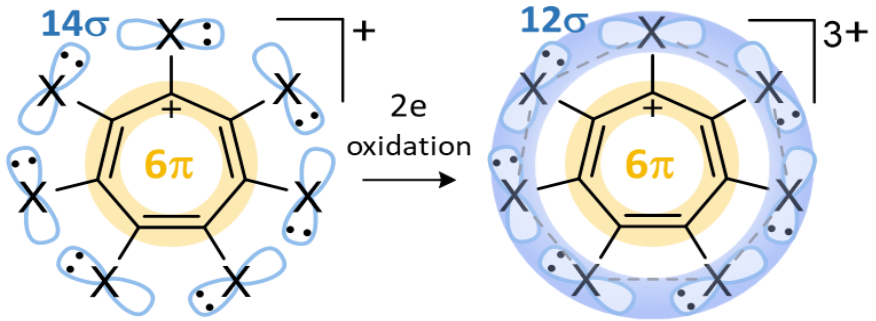
S. Furukawa, M. Fujita, Y. Kanatomi, M. Hatanaka, K. Morokuma, K. Ishamura, M. Saito, *Commun. Chem.* **2018**, *1*, 1-7.

X = Br, I, SeR, TeR

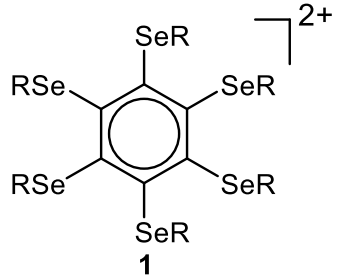
a) 6-Membered Ring



b) 7-Membered Ring



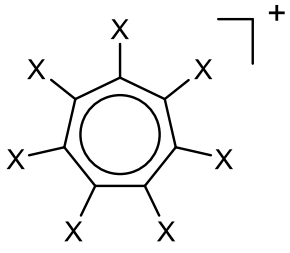
Previously reported double aromatic system



1

6π Hückel-A
10σ Hückel-A

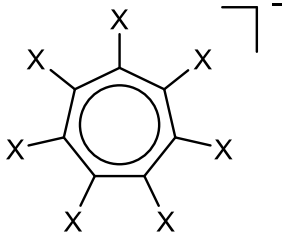
New proposed double aromatic systems:



2

X = Halogen or SePh

6π Hückel-A
14σ Hückel-A



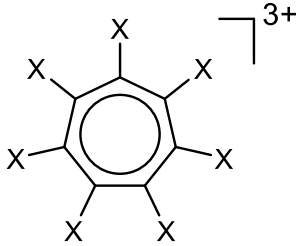
3

X = Br

8π AA
14σ Hückel-A
} In the lowest singlet state

or

8π Baird-A
14σ Hückel-A
} In the lowest triplet state



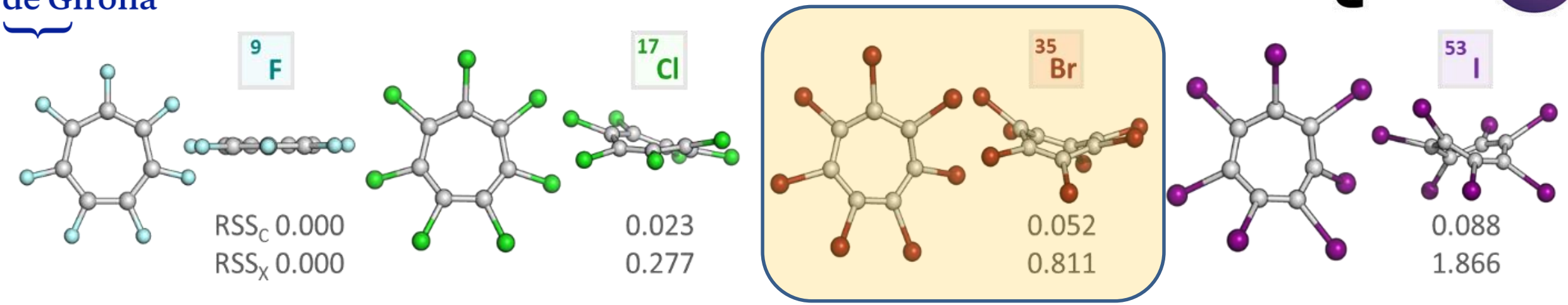
4

X = Br

6π Hückel-A
12σ AA
} In the lowest singlet state

or

6π Hückel-A
12σ Baird-A
} In the lowest triplet state

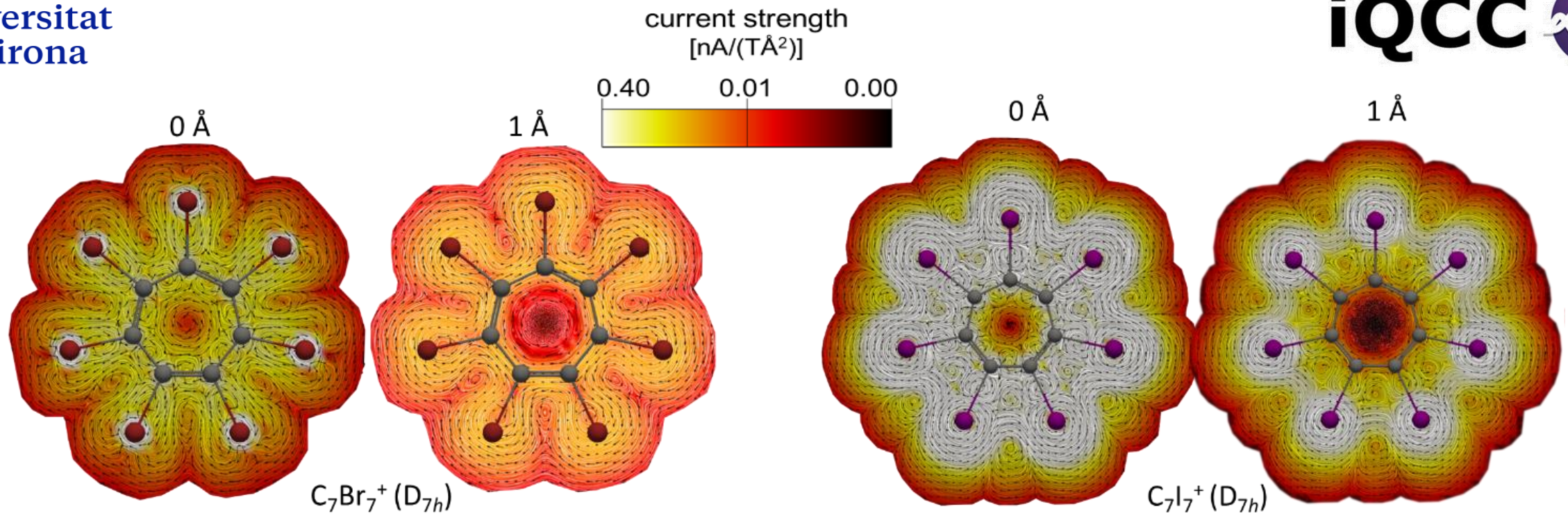


Fully optimized $^1C_7X_7^+$ (X = F, Cl, Br, and I) geometries using **BLYP/6-311+G(d,p)~SDD(I)** and the planarity Root-Summed-Square (RSS) index

i) X = Br is preferred over X = I to avoid excessive steric congestion that will result in ring puckering
ii) X = Br is preferred to X = Cl because the Br atom has more diffuse *4p* orbitals that can lead to better overlaps.

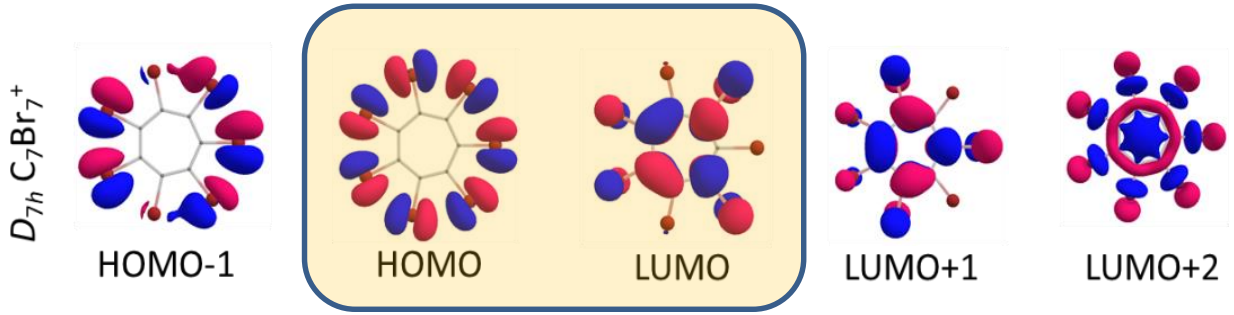
$C_7Br_7^+$ $\rightarrow$ MCI_C=0.0210 e; π-$EDDB_C$ = 3.800; $NICS(1)_{zz}$ = –10.9 ppm; MCI_{Br} = 0.000 e; σ-$EDDB_{Br}$ = 0.230 e

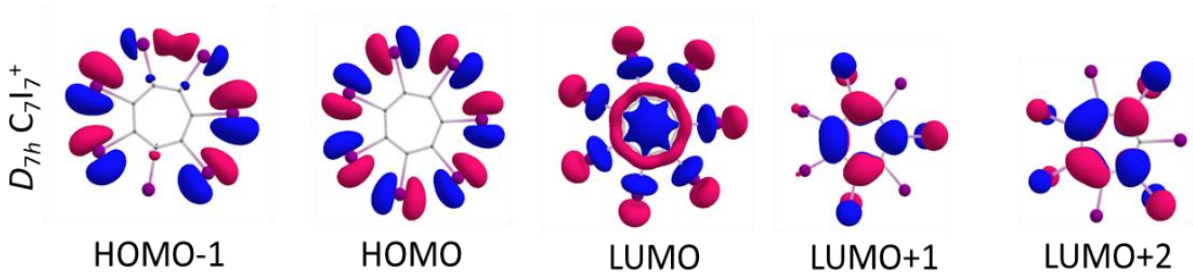
S. Escayola, N. Proos Vedin, A. Poater, H. Ottosson, M. Solà. *J. Phys. Org. Chem.* **2023**, *36*, e4447



$NICS(1)_{zz}$ = –12.0 ppm; MCI = 0.0238 e

$NICS(1)_{zz}$ = 27.9 ppm; MCI = 0.0291 e





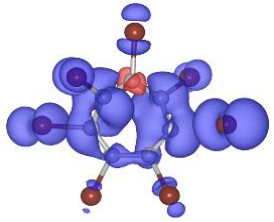
BLYP/6-311+G(d,p)~SDD(I)

$^{1}C_7Br_7^{+}$ → MCI_C=0.0210 e; π-$EDDB_C$ = 3.800; $NICS(1)_{zz}$ = –10.9 ppm; MCI_{Br} = 0.000 e; σ-$EDDB_{Br}$ = 0.230 e

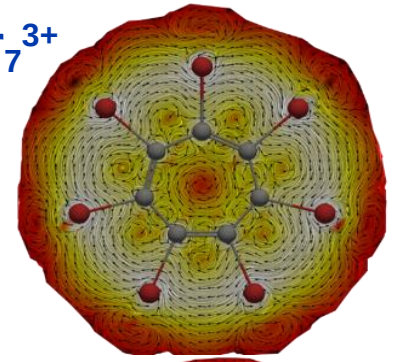
$^{1}C_7Br_7^{-}$ → MCI_C=0.0080 e; π-$EDDB_C$ = 2.327; MCI_{Br} = 0.000 e; σ-$EDDB_{Br}$ = 0.180 e

$^{3}C_7Br_7^{-}$→ MCI_C=0.0121 e; π-$EDDB_C$ = 2.336; MCI_{Br} = 0.000 e; σ-$EDDB_{Br}$ = 0.314 e

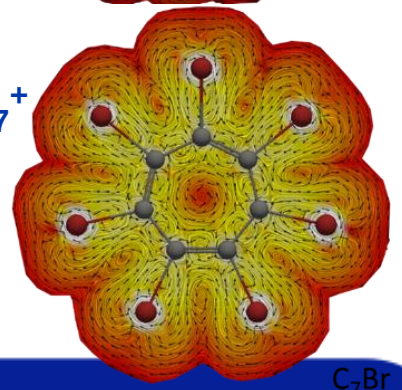
$^{3}C_7Br_7^{3+}$ → MCI_C=0.0246 e; π-$EDDB_C$ = 4.303; MCI_{Br} = 0.002 e; σ-$EDDB_{Br}$ = 2.626 e



$^{3}C_7Br_7^{3+}$

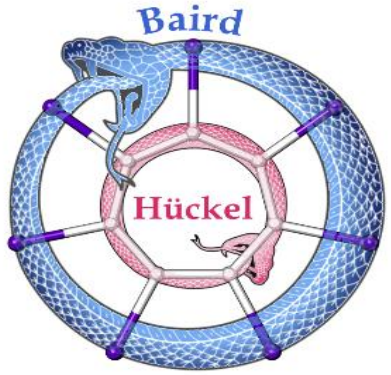


$^{1}C_7Br_7^{+}$

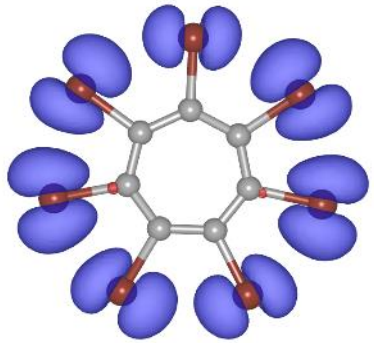


6π Hückel aromatic

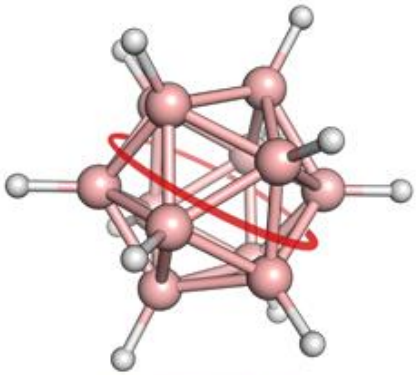
$^{3}C_7Br_7^{3+}$



12π Baird weakly aromatic

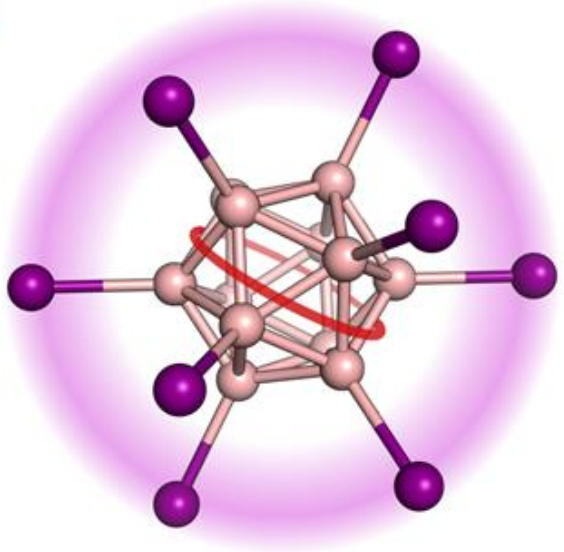


Closo Boranes, $[B_nX_n]^{2-}$



$[B_{12}H_{12}]^{2-}$
3D-aromatic

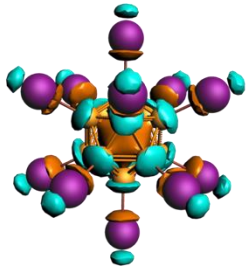
addition of an external l-shell



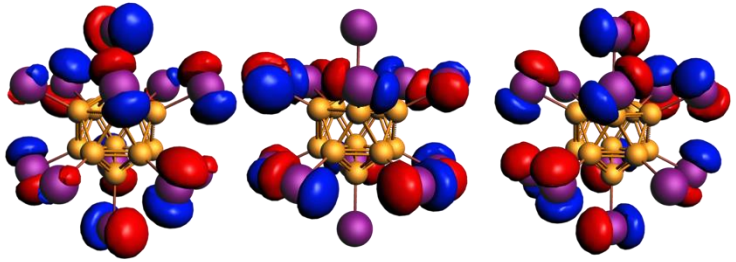
$[B_{12}I_{12}]$ and $[B_{12}I_{12}]^{2+}$
doubly 3D-aromatic ?

magnetic ✓
electronic ~
energetic ✗

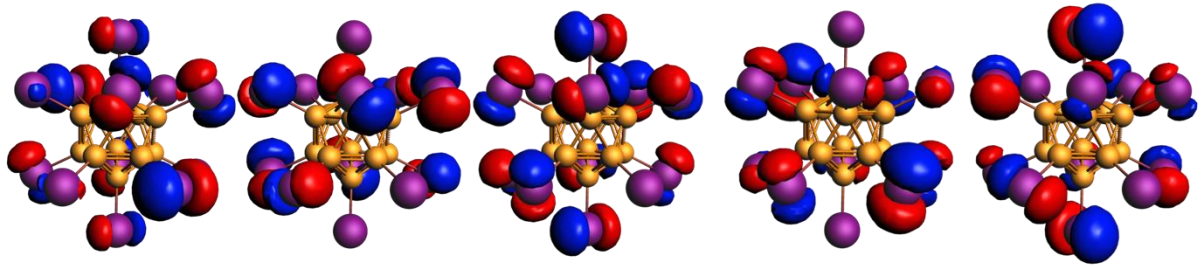
Molecular Orbitals, $[B_{12}I_{12}]^{2-}$



LUMO, 2.17 eV



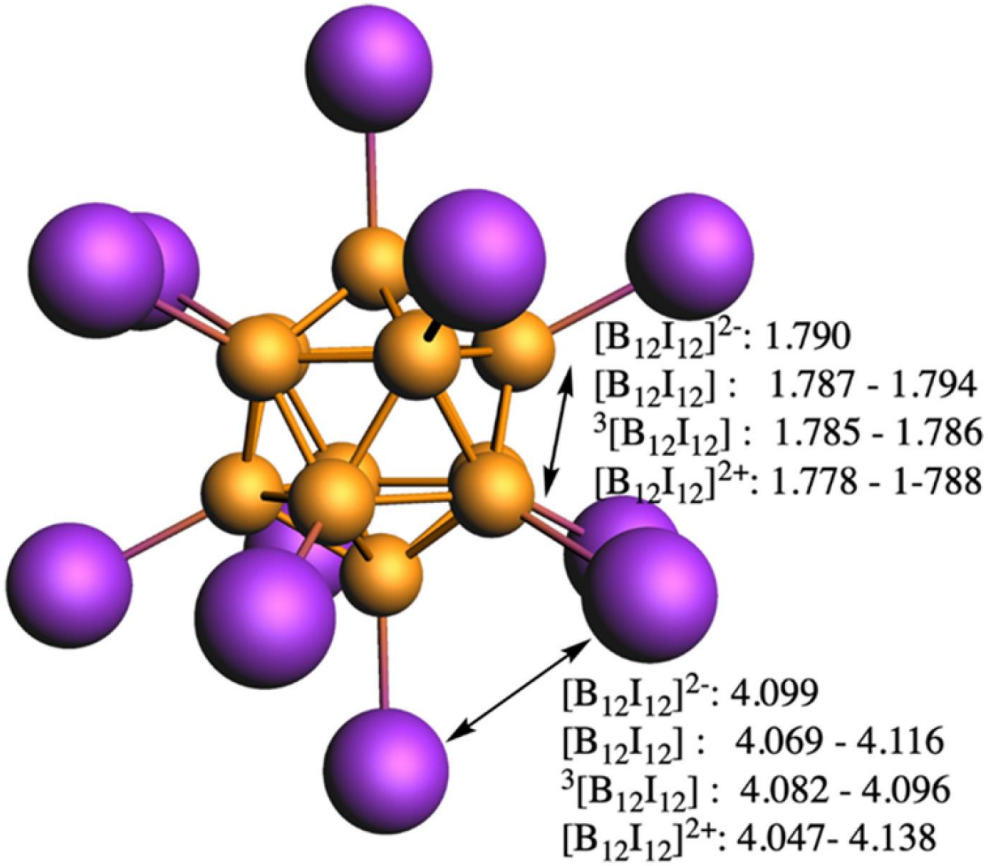
HOMO, 0.06 eV

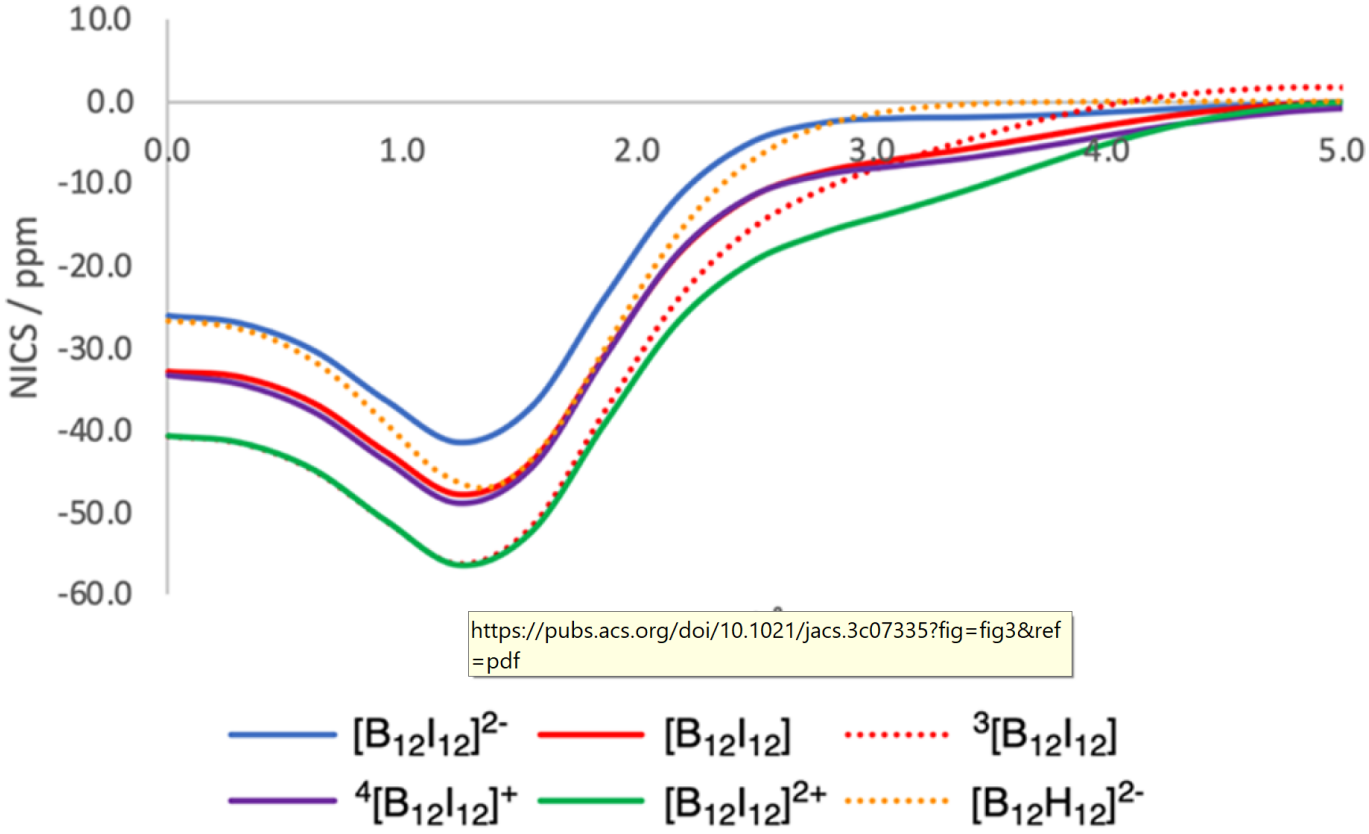


HOMO-1, 0.46 eV

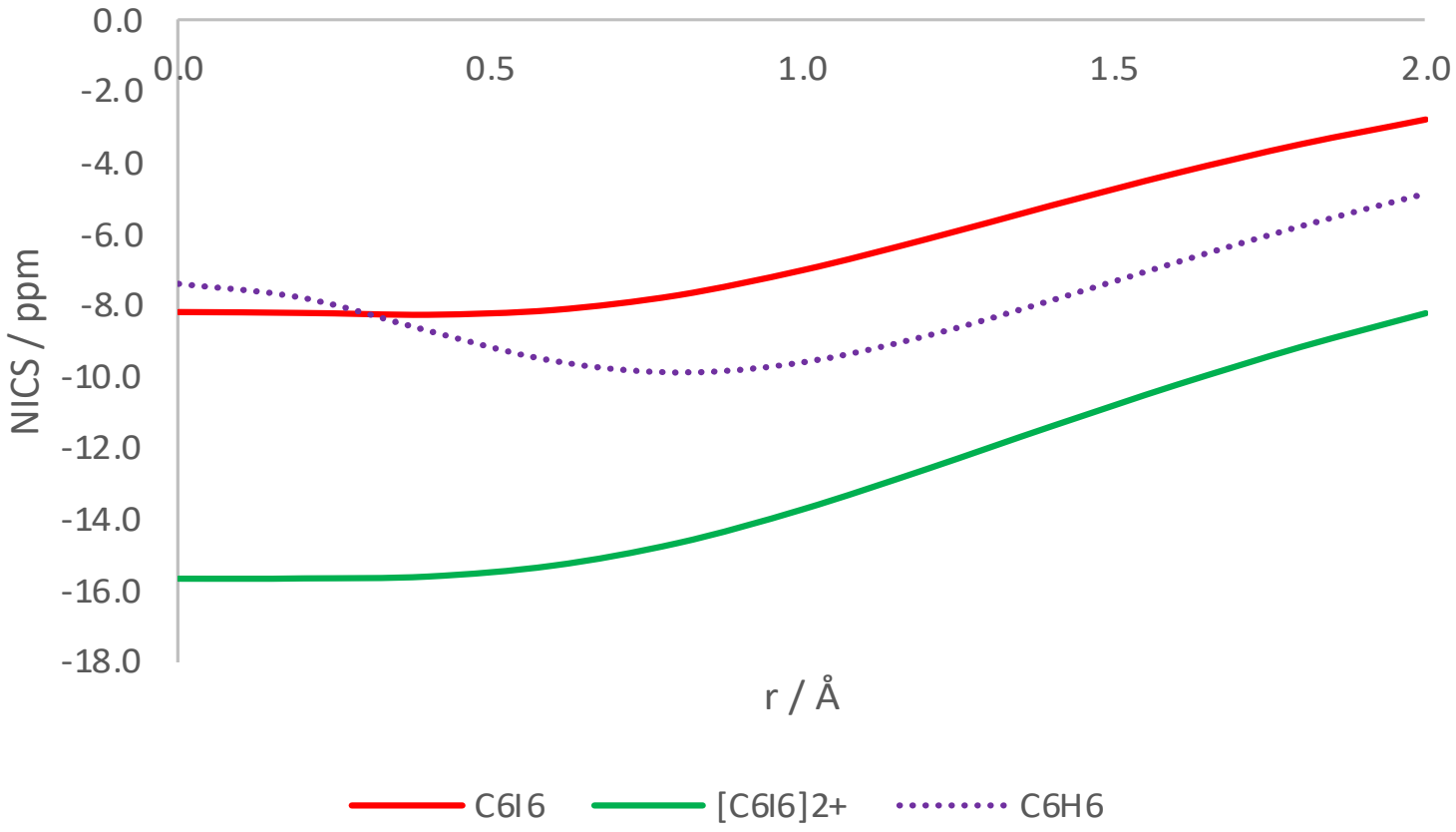
ZORA-BLYP-D3(BJ)/TZ2P

3D-double aromaticity



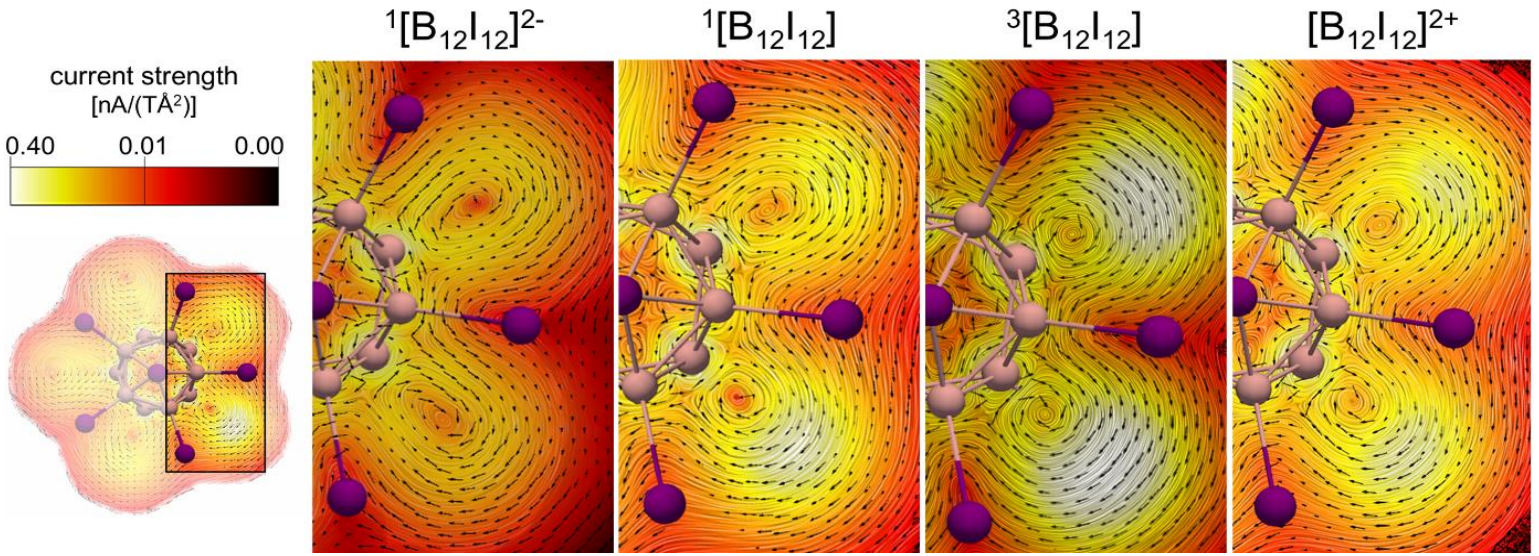


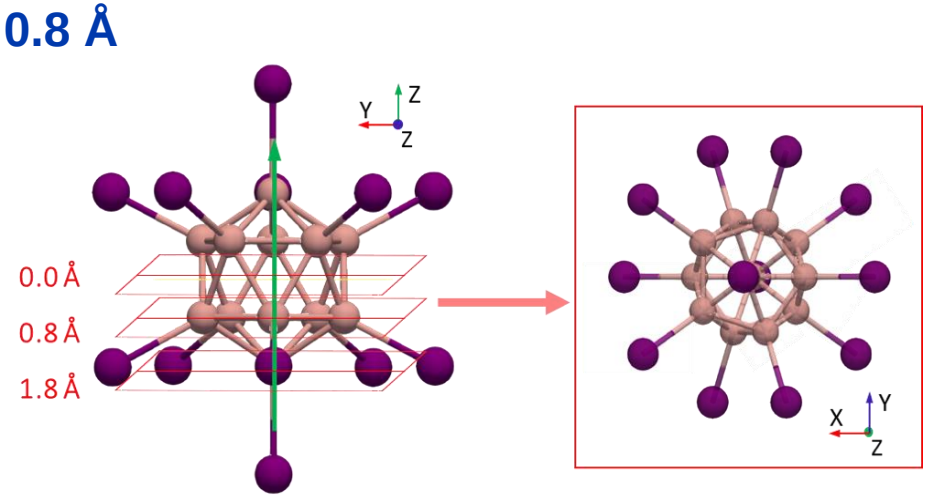
3D-double aromaticity

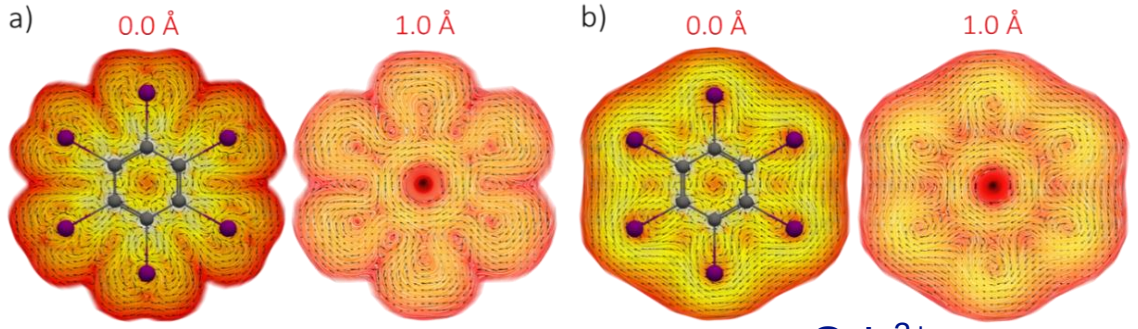


3D-double aromaticity

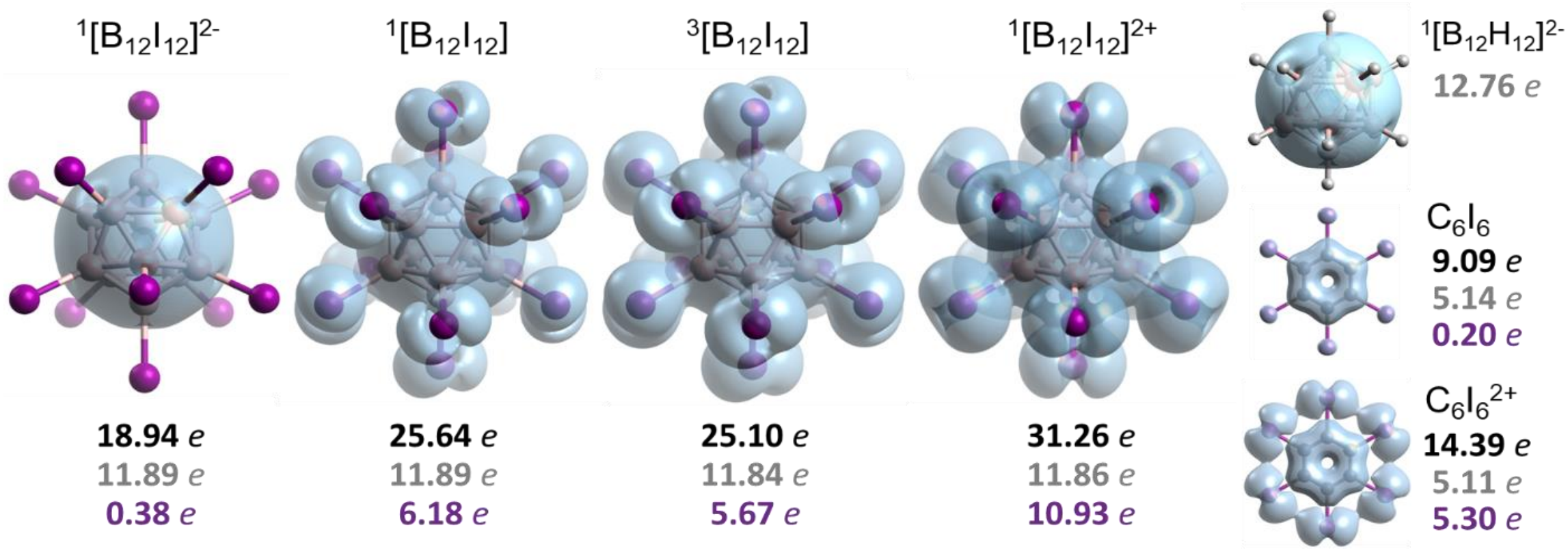
B3LYP/6-311++G**~LANL2DZ//ZORA-BLYP-D3(BJ)/TZ2P







3D-double aromaticity (EDDB)



B3LYP/6-311++G~LANL2DZ//ZORA-BLYP-D3(BJ)/TZ2P**

3D-double aromaticity (ASE)

$[C_6I_6]^{2+} + C_6H_6 \rightarrow [C_6H_3I_3]^{2+} + C_6H_3I_3$ $\Delta G = 37.1$ kcal/mol

(mirar d'in surten els electrons del $[C_6H_3I_3]^{2+}$)

$B_{12}I_{12} + [B_{12}H_{12}]^{2-} \rightarrow B_{12}H_6I_6 + B_{12}H_6I_6^{2-}$ $\Delta G = -37.5$ kcal/mol

$[B_{12}I_{12}]^{2+} + [B_{12}H_{12}]^{2-} \rightarrow [B_{12}H_6I_6]^{2+} + [B_{12}H_6I_6]^{2-}$ $\Delta G = -2.8$ kcal/mol

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

"**Aromaticity is a manifestation of electron delocalization in closed circuits, either in two or three dimensions,** which results in **energy lowering**, often quite substantial, and a variety of unusual chemical and physical properties. These include a tendency toward bond length equalization, unusual reactivity, and characteristic spectroscopic features as well as distinctive magnetic properties related to strong induced ring currents."

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

Aromaticity is a complex phenomenon; aromatic compounds have many interesting properties, but two are essential, **electron delocalization** and **energetic stabilization**. A lack of one of these two precludes the existence of aromaticity.

Cyclo[18]carbon

Universitat

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Achieving Adaptive Aromaticity in Cyclo[10]carbon by Screening Cyclo[n]carbon (n=8–24)

Chenshu Dai, Dandan Chen, Prof. Dr. Jun Zhu

First published: 28 May 2020 | https://doi.org/10.1002/asia.202000528 | Citations: 43

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Double Aromaticity and Ring Currents in All-Carbon Rings

Patrick W. Fowler,*[a] Noriyuki Mizoguchi,[b] David E. Bean,[a] and Remco W. A. Havenith[c]

Abstract: Double aromaticity of neutral, planar rings of carbon atoms is demonstrated through visualisation of the induced ring currents, mapped at the ipsocentric B3LYP/6-31G(d)//B3LYP/6-31G(d) level for species C_6 to C_{30}, with onset of delocalised current in the in-plane π system at C_{10}/C_{11}. Both in-plane and conventional out-of-plane π systems have diatropic/paratropic current in accordance with the Hückel rule, with $4m+2$ occupation of the out-of-plane π system taking precedence, as predicted by simple nesting of Frost–Musulin diagrams. The current-density maps show characteristic double-doughnut and double-track topographies for out-of-plane and in-plane ring currents, respectively, both governed by a common framework of angular momentum rules.

Keywords: aromaticity · carbon · cluster compounds · density functional calculations · magnetic properties · ring currents

Issue 17, 2020

From the journal:
Physical Chemistry Chemical Physics

Induced magnetic field in sp-hybridized carbon rings: analysis of double aromaticity and antiaromaticity in cyclo[2*N*]carbon allotropes†

Nickolas D. Charistos *a and Alvaro Muñoz-Castro *b

Author affiliations

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Cyclo[18]carbon: Insight into Electronic Structure, Aromaticity, and Surface Coupling

Glib V. Baryshnikov*, Rashid R. Valiev, Artem V. Kuklin, Dage Sundholm, and Hans Ågren*

Cite this: *J. Phys. Chem. Lett.* 2019, 10, 21, 6701–6705
Publication Date: October 14, 2019
https://doi.org/10.1021/acs.jpclett.9b02815

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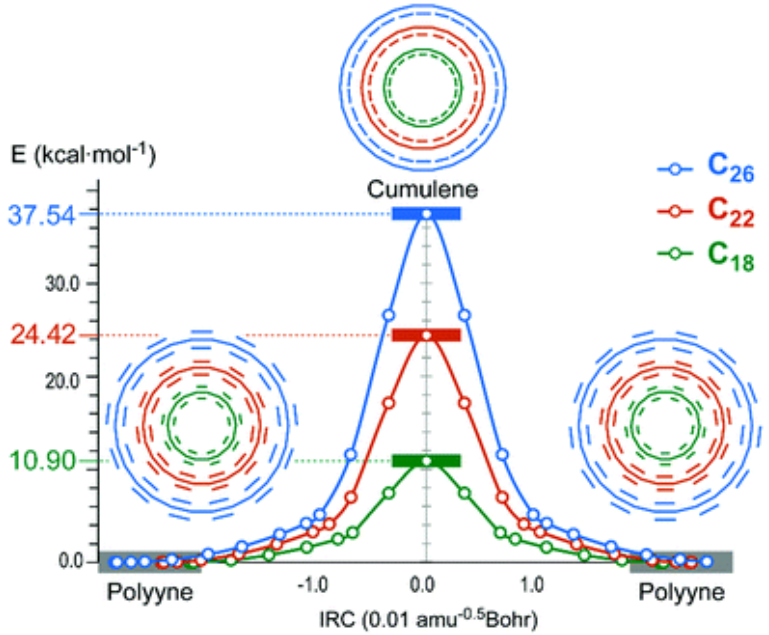
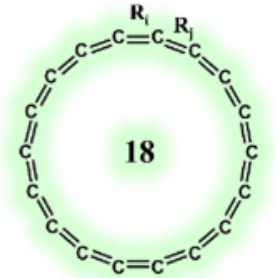
PF talk → Aromaticity is a magnetic phenomenon



FMB talk → many π-orbitals in favor of localization

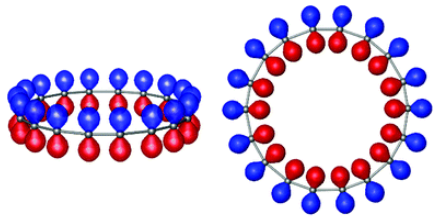
IR talk



Cumulenic C_{18} $R_i = R_j$

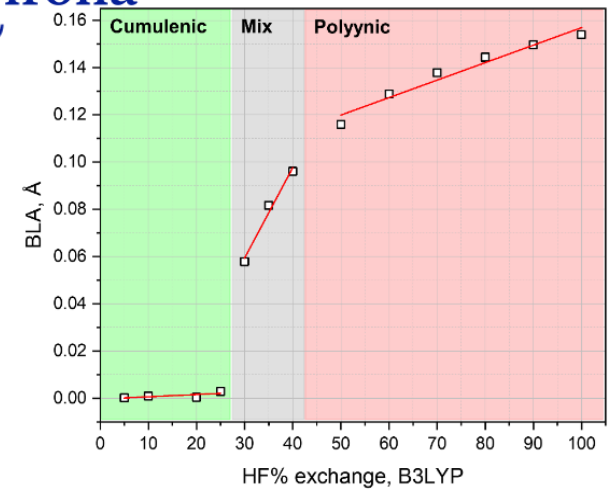
Polyynic C_{18} $R_i \neq R_j$

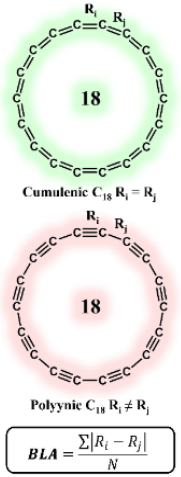
$$BLA = \frac{\sum |R_i - R_j|}{N}$$

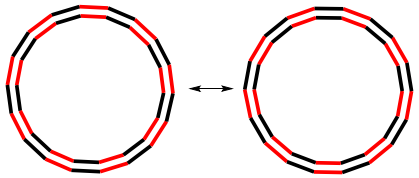


π_{out} π_{in}

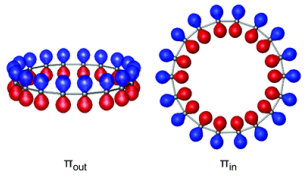
Cyclo[18]carbon

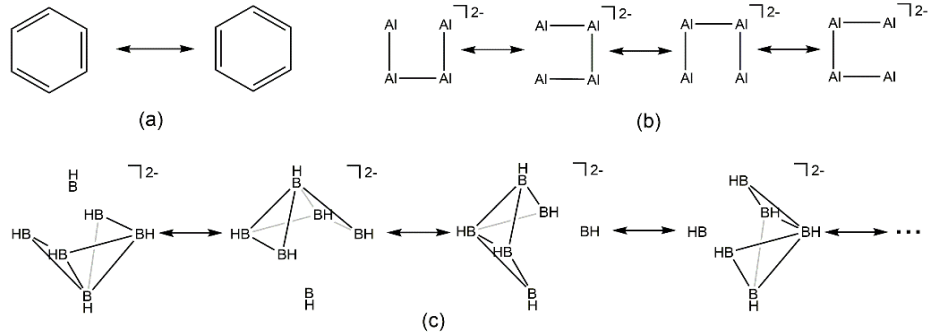






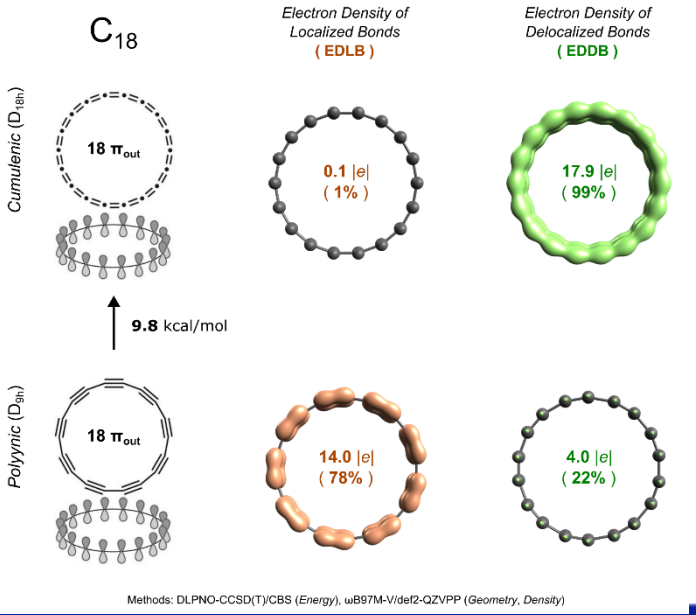
Cumulenic structure

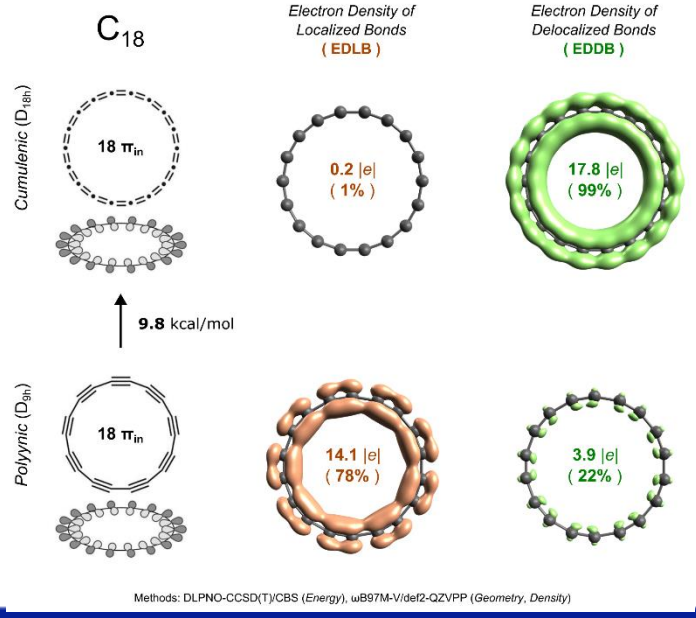


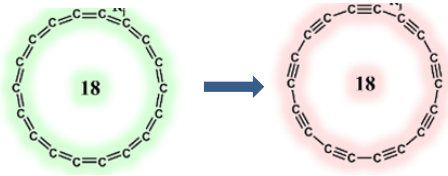


Dr. Dariusz Szczepanik

A. J. Stasyuk, O. A. Stasyuk, M. Solà and A. A. Voityuk *Chem. Commun.* **2020**, *56*, 352







ASE = -9.8 kcal/mol

Solà, M.; Szczepanik, D. W., to be submitted

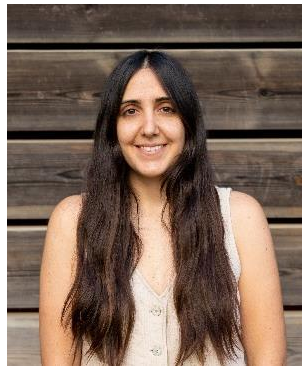
CONCLUSIONS

- Among the systems studied only $C_7Br_7^{3+}$ in its triplet state with an internal Hückel aromatic tropylium ring and an external incipient Baird aromatic Br_7 ring shows double π- and σ-aromaticity.

- Magnetic and electronic descriptors of aromaticity suggest the presence of double aromaticity in $[B_{12}I_{12}]^{0/2+}$. However, delocalization in the I_{12} shell does not contribute to any stabilization of the system. Therefore, $[B_{12}I_{12}]^{0/2+}$ cannot be considered doubly 3D-aromatic.

- A lack of electron delocalization or energetic stabilization precludes the existence of aromaticity.

ACKNOWLEDGMENTS



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Prof. Jordi Poater (UB)

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Prof. Francesc Teixidor (ICMAB)

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