Transmission of spin-polarization by π-orbitals: an approach to assessing its effect on NMR spin–spin coupling and EPR hyperfine structure

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- *Dedicated to the memory of Prof. Paul von Ragué Schleyer*

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- Michael Bühl
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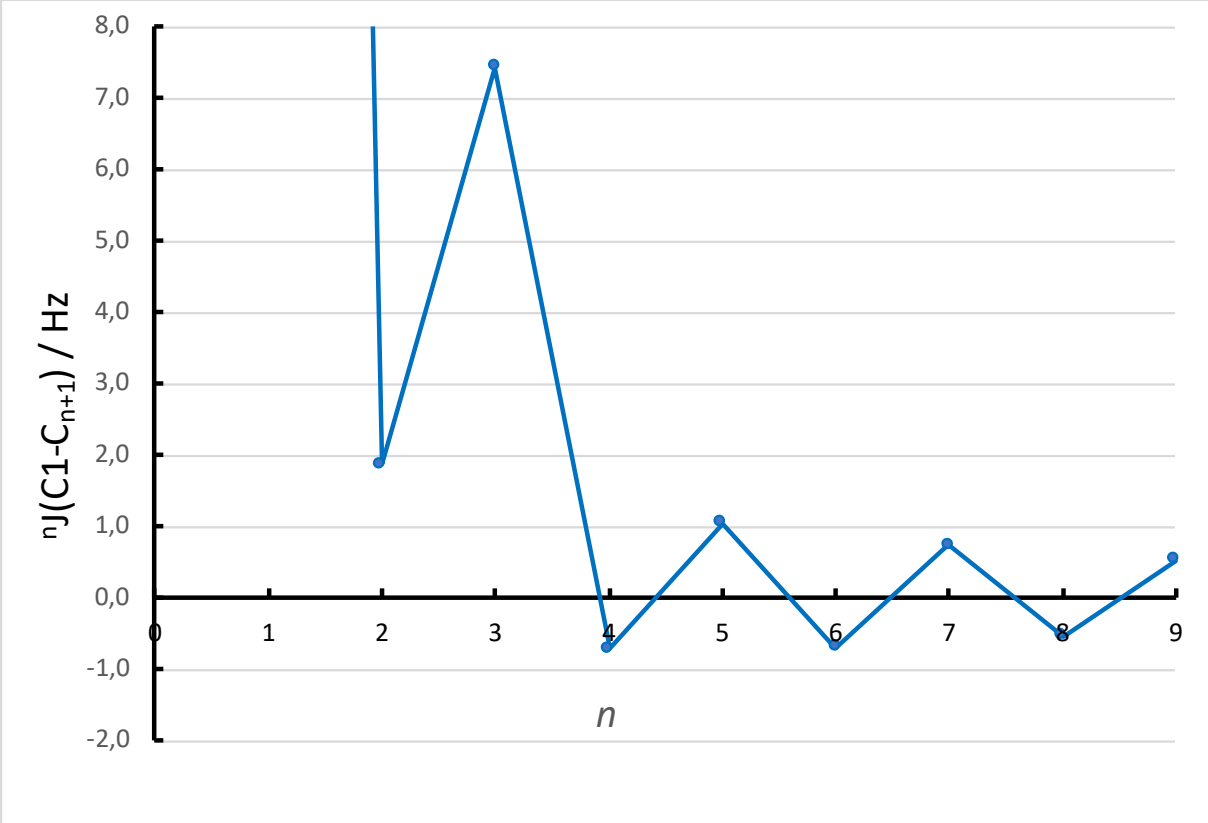
Frequently asked questions

- What is the role of π-MOs in NMR spin–spin coupling?
- Which effects govern the propagation of spin-polarization through π-MOs?
- Why there is a sign-alternation pattern of spin-polarization going via π-MOs?

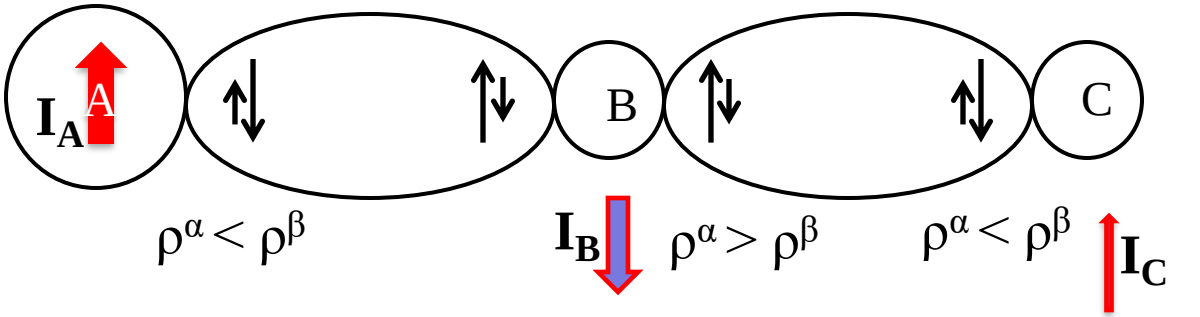
$$J_{AB} \sim \sum_{k,a} \frac{\left\langle \varphi_k^0 \middle| \hat{H}_{FC}(A) \middle| \varphi_a^0 \right\rangle \left\langle \varphi_a^0 \middle| \hat{H}_{FC}(B) \middle| \varphi_k^0 \right\rangle}{\varepsilon_k - \varepsilon_a}$$

$$H_{FC}(A) = \frac{8\pi\alpha^2}{3} \delta(r_{Ai}) \cdot \hat{S}_{iz}$$



$^{n}J_{FC}(C_1–C_{n+1})$ in 1,3,5,7,9-decapentaene as a function of the number of bonds separating the two carbons (in Hz).

The Dirac vector model for spin-polarization induced by the nuclear magnetic moment (FC mechanism)



*E. Duval, S. Koide, Phys. Letters, **1964**, 8, 314*

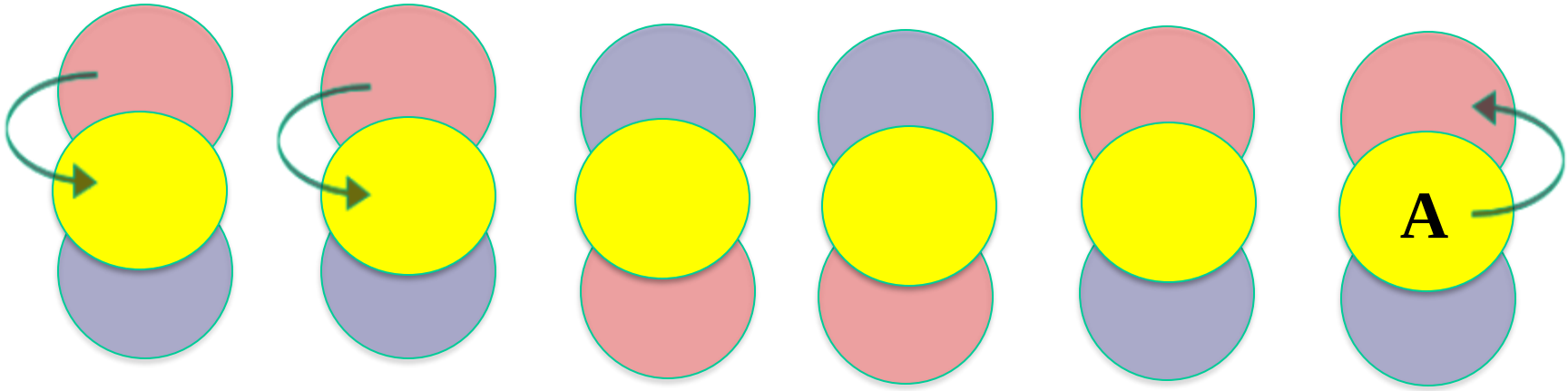
We start with a close shell system !!!

$$H_{FC} = \frac{8\pi\alpha^2}{3}\,\delta(r_{Ni})\cdot\hat{S}_{iz}$$

$$\mathbf{K_{ij}\ ,\ V_{xc}}$$

In case of GGA functionals

$$\boldsymbol{V_{xc}(\rho\ ,\rho^{\alpha-\beta})}$$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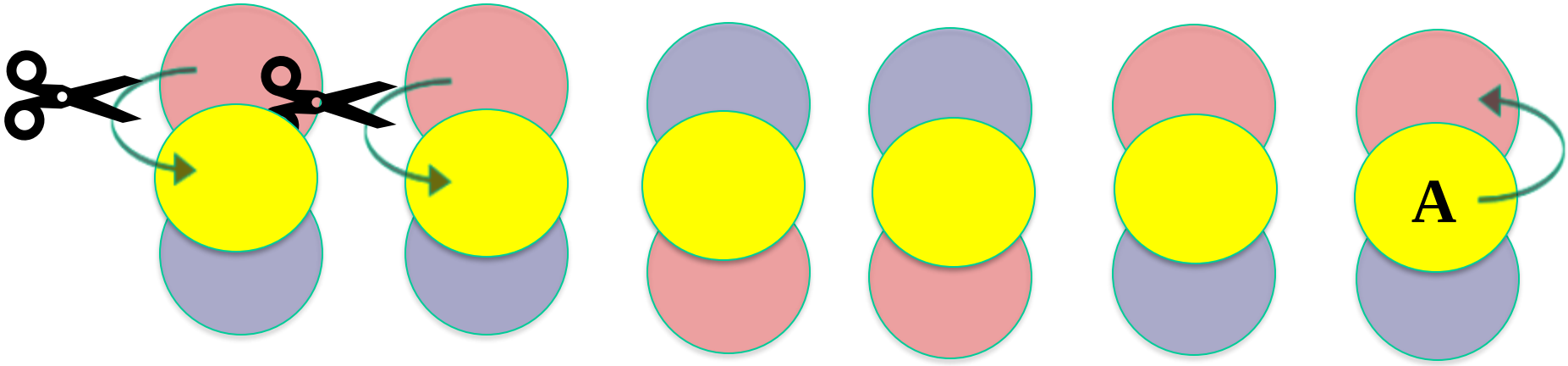
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$$H_{FC} = \frac{8\pi\alpha^2}{3}\,\delta(r_{Ni}) \cdot \hat{S}_{iz}$$

$$\mathbf{K_{ij}\ ,\ V_{xc}}$$

In case of GGA functionals

$$\boldsymbol{V_{xc}(\rho\ ,\rho^{\alpha-\beta})}$$

Contribution to V_{xc} from **π** MOs

$$\boldsymbol{V_{xc}(\rho)}$$

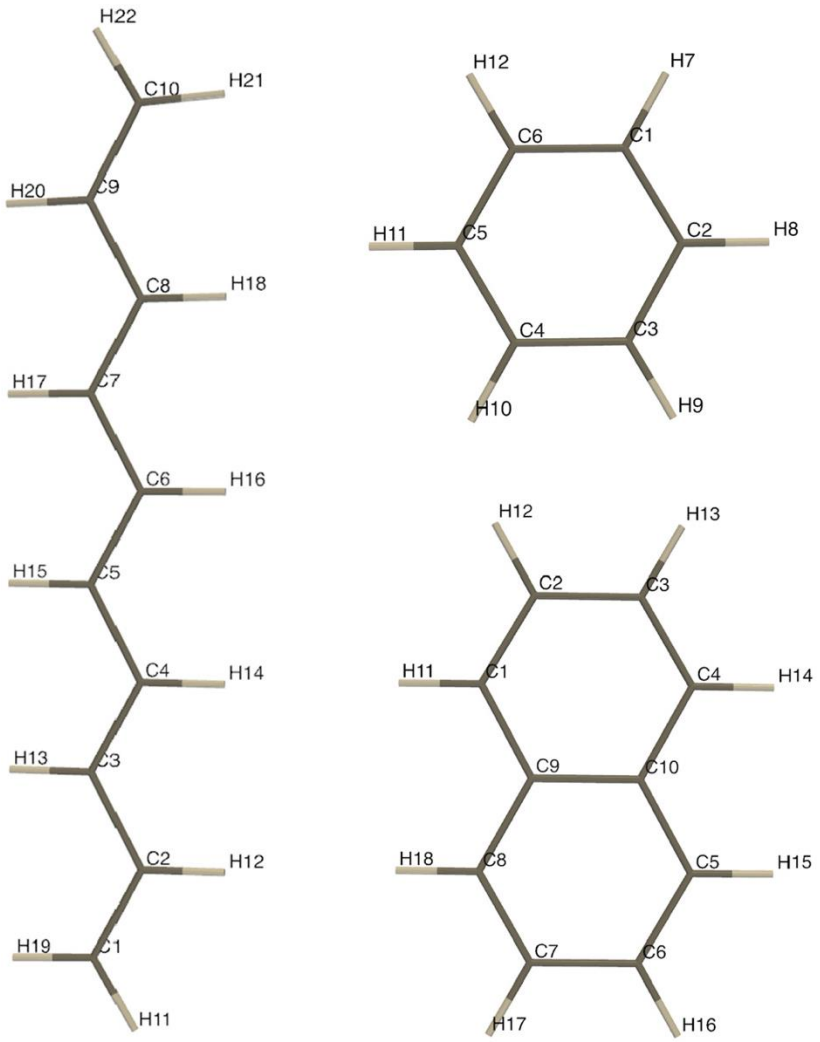


Fig. 1 Molecular structure and the numbering of atoms in 1,3,5,7,9-decapentaene (left), benzene (top right) and naphthalene (bottom right). The 1,3,5,7,9-decapentaene radical considered in this work is obtained from 1,3,5,7,9-decapentaene by removing atom H19

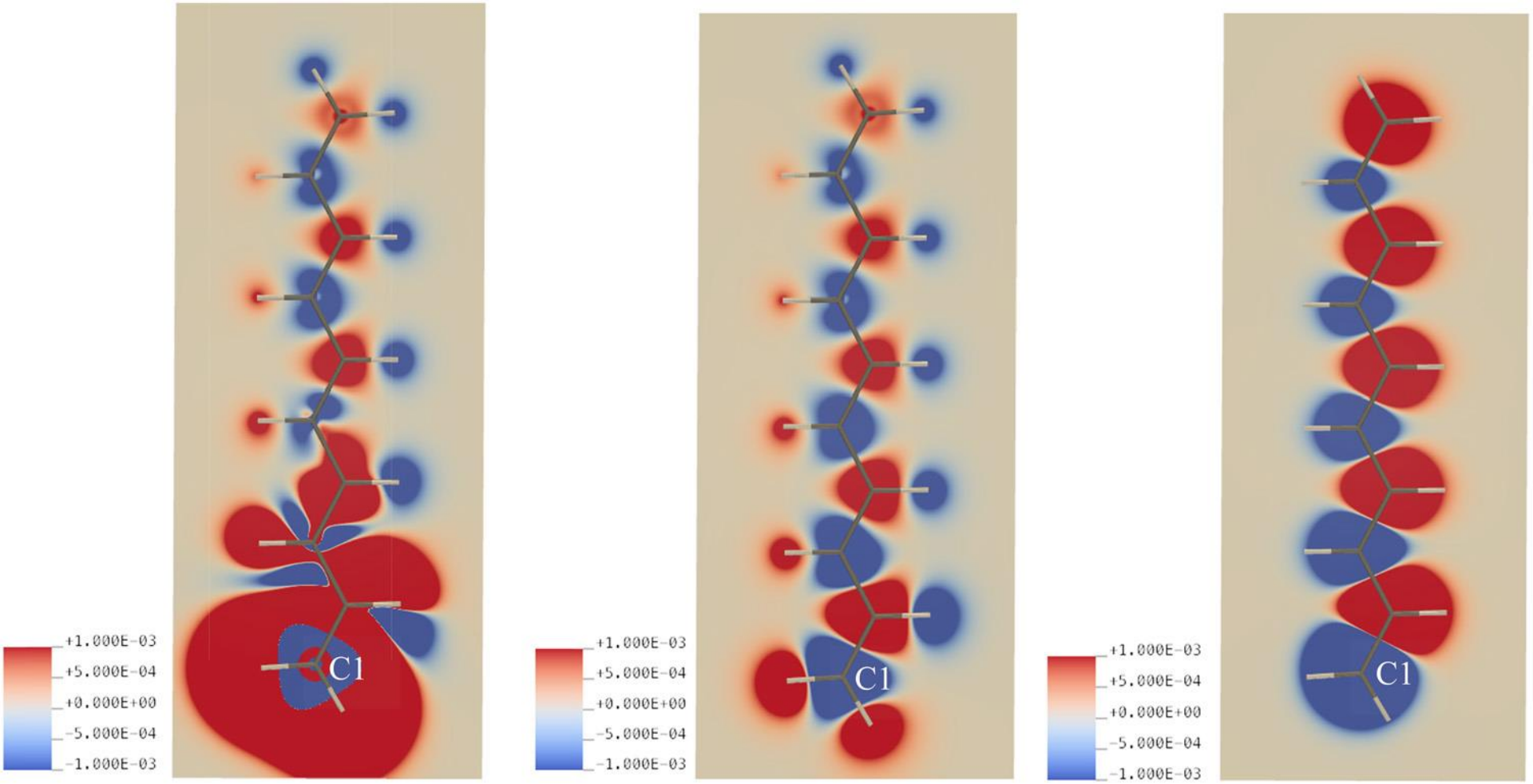


Fig. 3 The ***spin-density*** in 1,3,5,7,9-decapentaene induced by FC(C1) (color-coded according to the density values, given in a.u.).

Left: The total spin-density -- shown in the molecular plane.

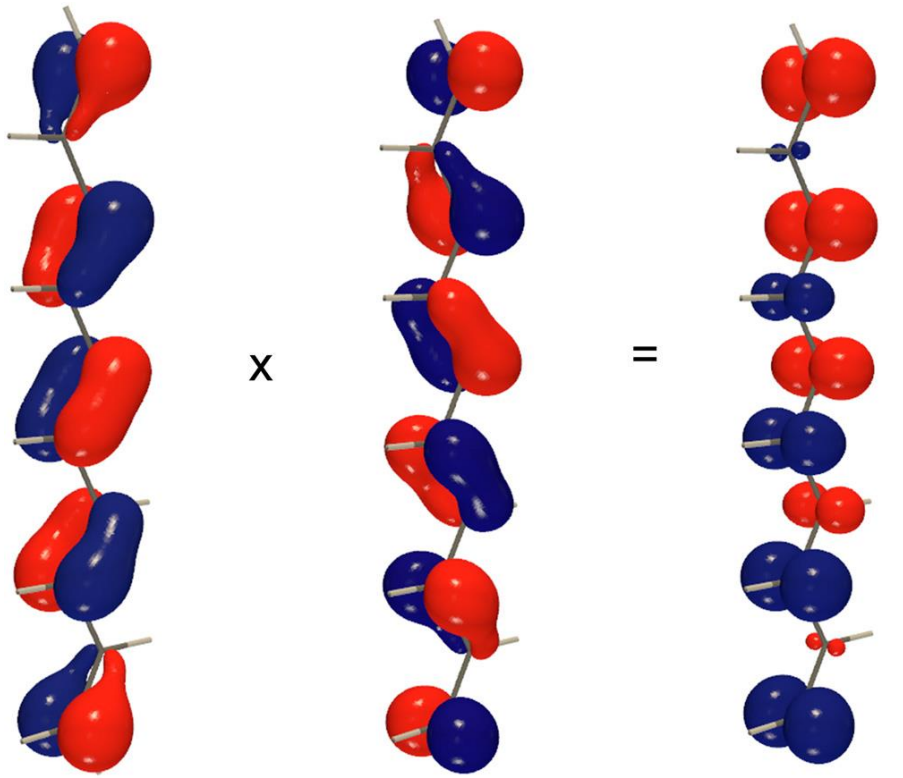
Middle: spin-polarization only due to the π-TSP effect (middle) -- shown in the molecular plane.

Right: spin-polarization of the group of π-orbitals -- shown in the plane 0.5 Å. below the molecular plane.

$$\pi'_\alpha \approx \pi + \lambda\pi^*$$

$$\pi'_\beta \approx \pi - \lambda\pi^*$$

$$\rho_\alpha - \rho_\beta \approx (\pi + \lambda\pi^*)^2 - (\pi - \lambda\pi^*)^2 = 4\lambda\,\pi\,\pi^*.$$



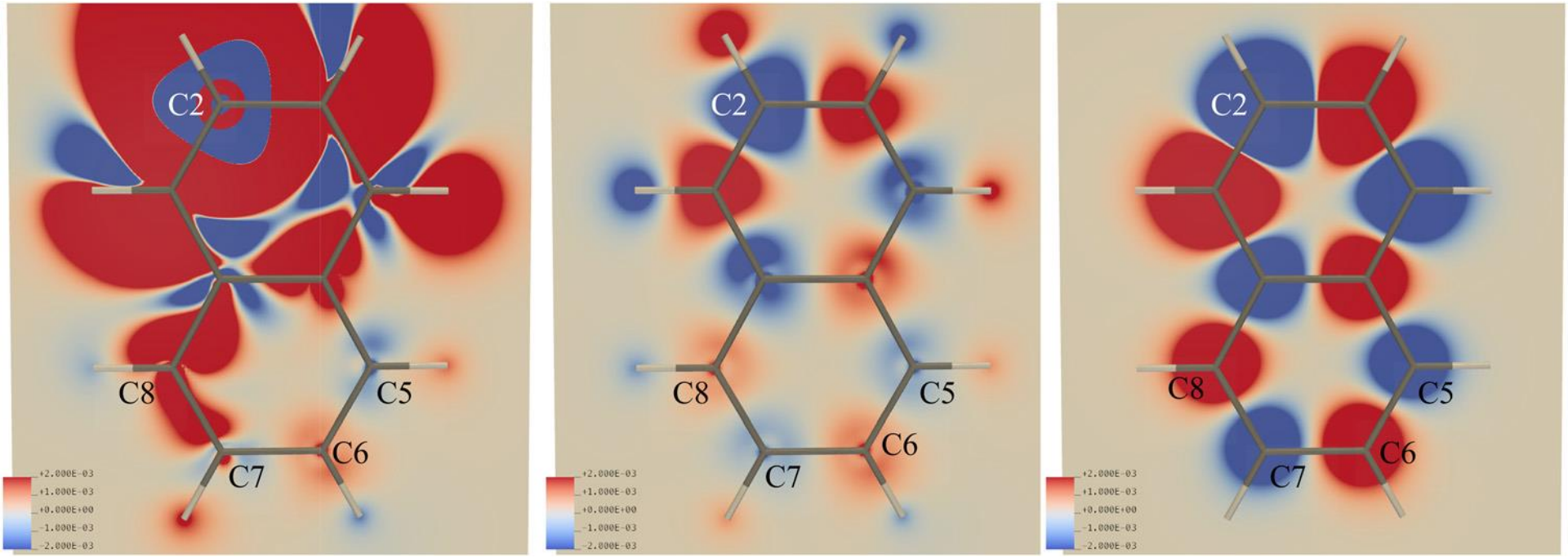


Fig. 6 The spin-density in naphthalene induced by FC(C2) (color-coded according to the density values, given in a.u.).

***Left**: the total spin-density (is shown in the molecular plane).*
***Middle**: spin-polarization only due to the π-TSP effect (is shown in the molecular plane).*
***Right**: the spin-polarization of the group of π-orbitals is shown in the plane 0.5 . below the molecular plane.*

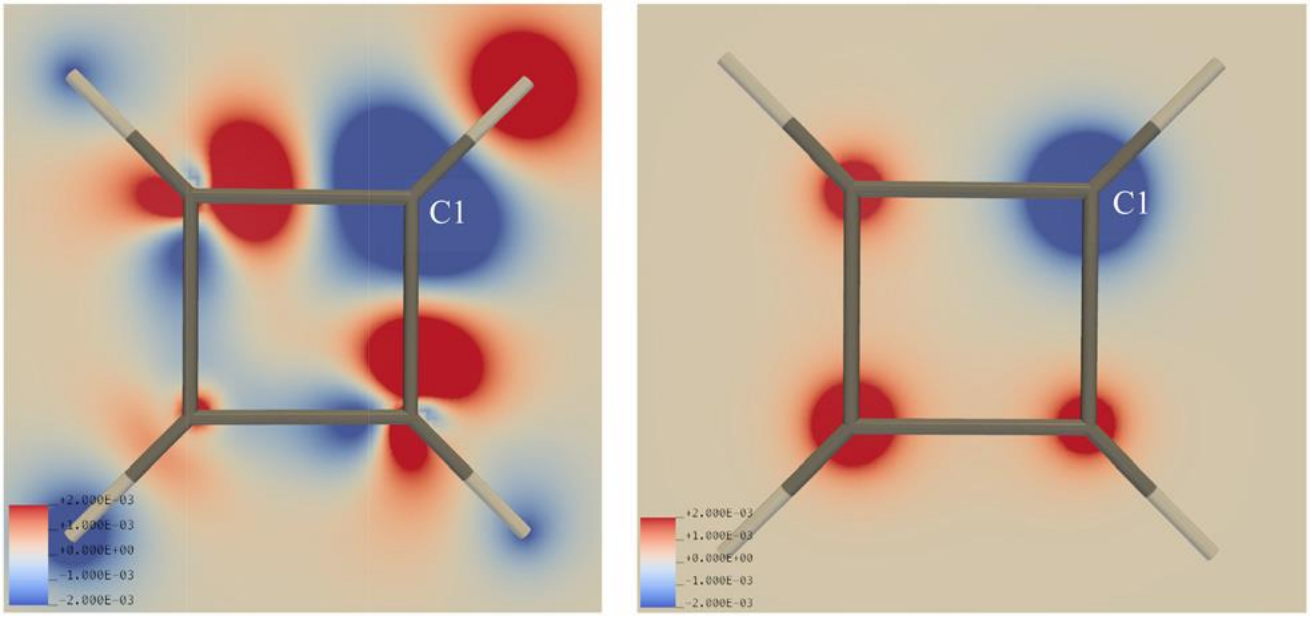
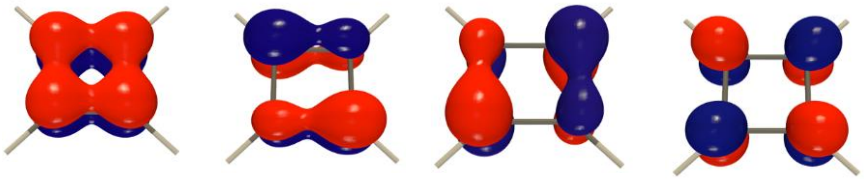


Fig. 7 The spin density in cyclobutadiene dication induced by FC(C1). Color-coded according to the density values given in a.u.

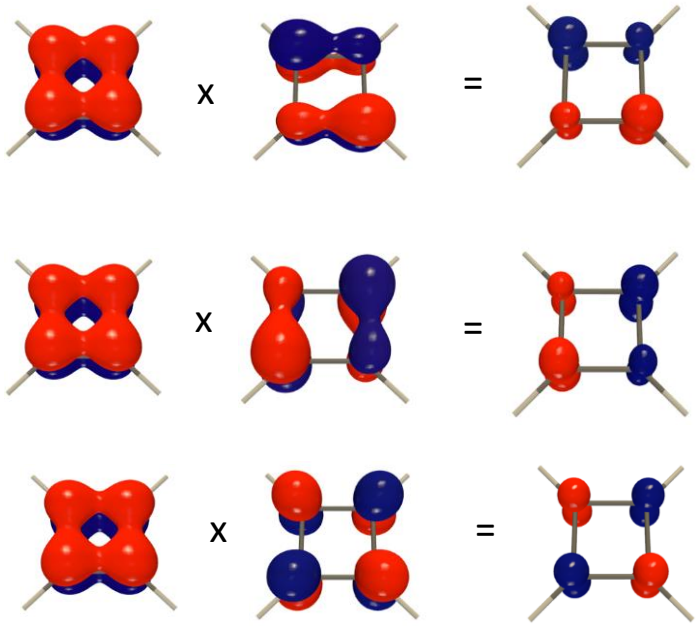
Left: The π-TSP effect on the spin density in cyclobutadiene dication induced by FC(C1)

Right: spin-polarization of the group of π-orbitals in the plane 0.5 Å below the molecular plane

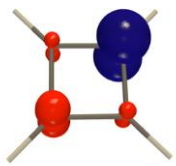


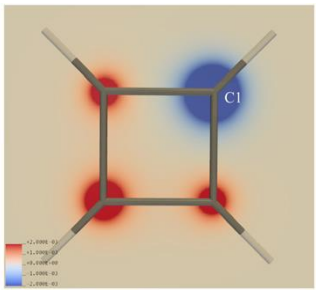
MO11 MO14 MO15 MO16

Figure S5. The occupied p-orbital (MO11) and the lowest vacant p-orbitals (MO14, MO15 and MO16) of a cyclobutadienyl dication. The isosurface value 0.1 a.u. .



MO11 x MO14 + MO11 x MO15 + MO11 x MO16 =





Conclusions

- ✓ A new DFT-based approach assessing the effect of the transmission of spin-polarization by π-orbitals (π-TSP) was developed.
- ✓ This approach is applicable to the analysis of molecular properties that depend on the effects of spin-polarization (i.e, NMR spin-spin couplings, EPR hyperfine couplings, etc.).
- ✓ It is based on simple switching off the contribution of π-MOs to the spin polarization.
- ✓ To the best of our knowledge, the sign alternation of the π-TSP effect on spin-spin couplings was explained for the first time based on perturbation theory and Hund's rule.
- ✓ We have also identified exceptions to this pattern, where – for identifiable reasons – spin-polarization delocalization effects occur across a cyclic π-system, interfering with the usual sign-alternating pattern.

Hyperfine structure (open shell systems)

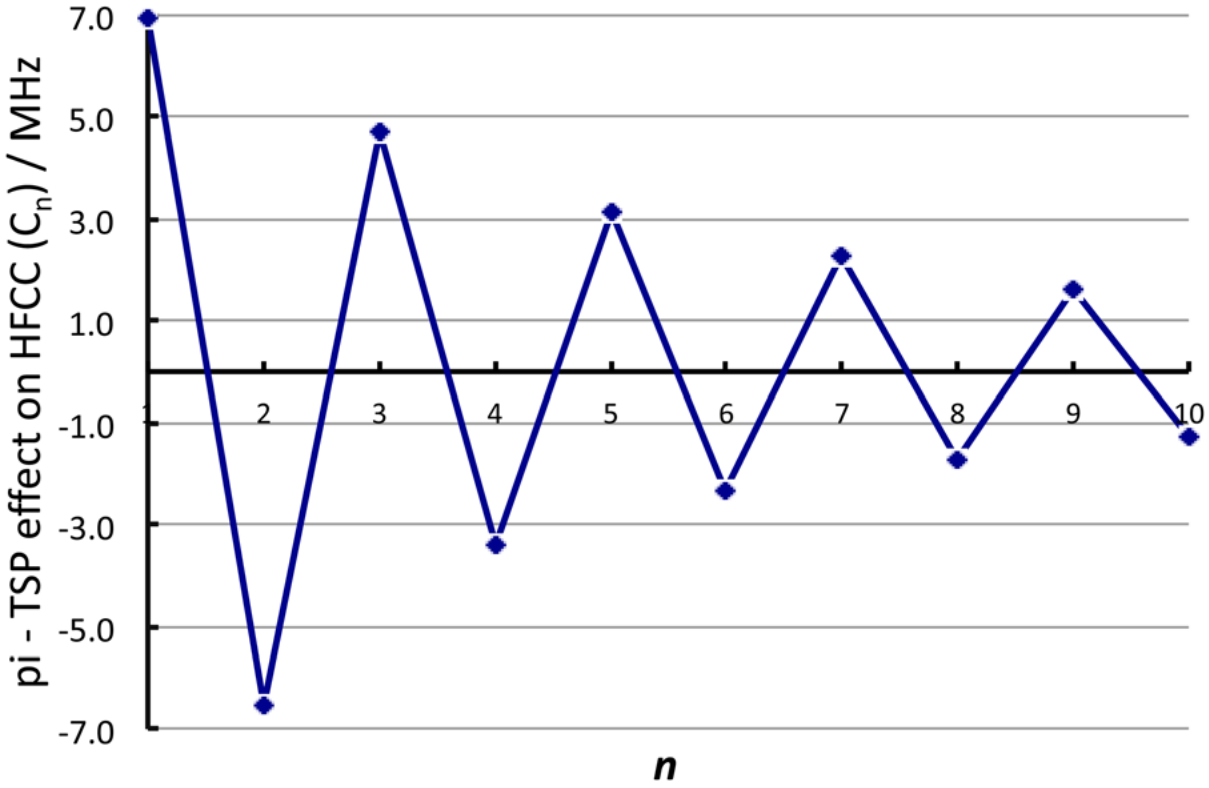


Fig. 10 The π -TSP effect on ^{13}C HFCC (in MHz) in the 1,3,5,7,9-decapentaen-1-yl radical. The values on the horizontal axis correspond to the numbering of carbons in Fig. 1, left.

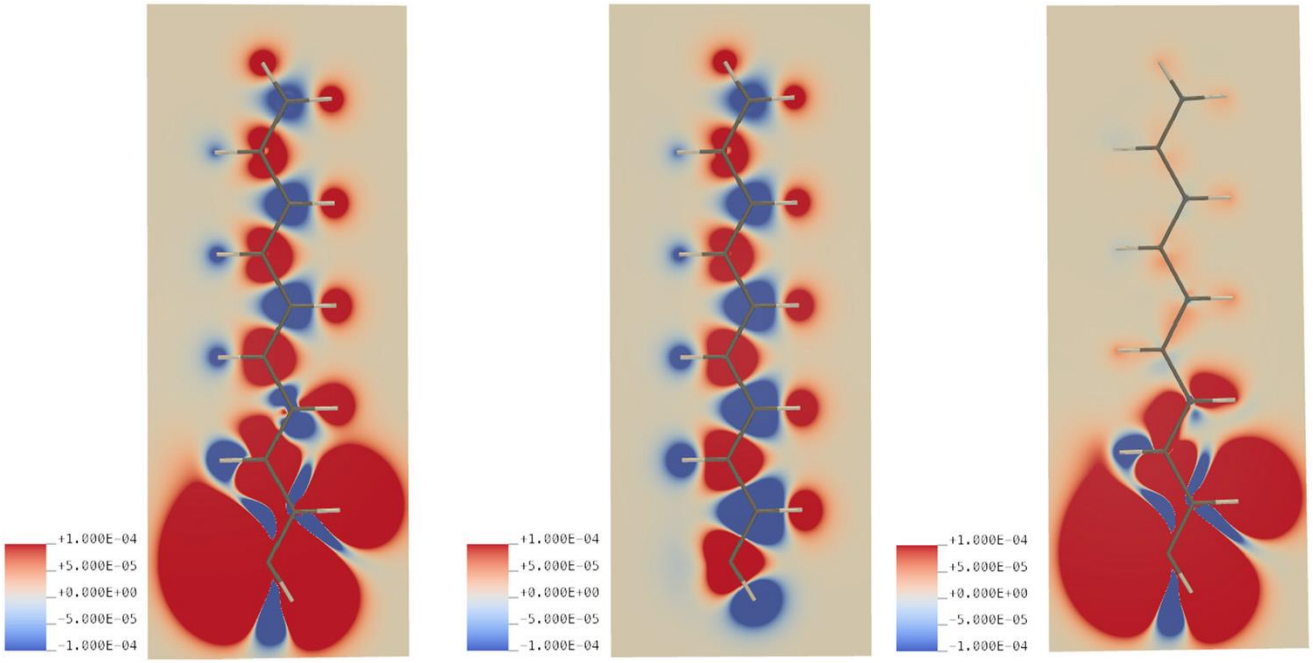


Fig. 11 The spin-density of the 1,3,5,7,9-decapentaene-1-yl radical (in the radical plane).

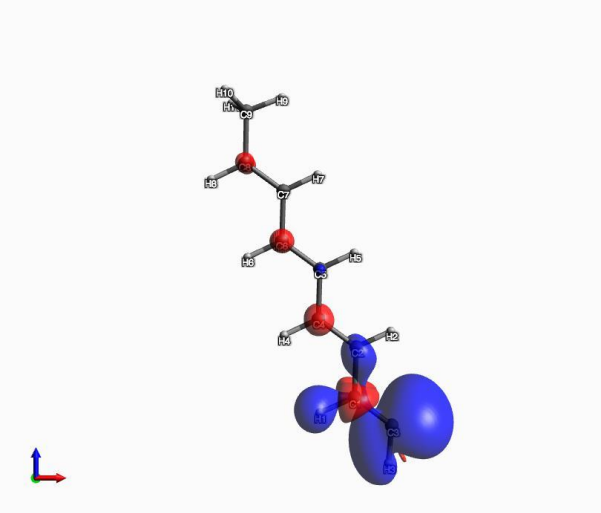
Left: The total spin-density of the 1,3,5,7,9-decapentaene-1-yl radical in the radical plane.

Middle: the spin-density due-to the π -TSP effect .

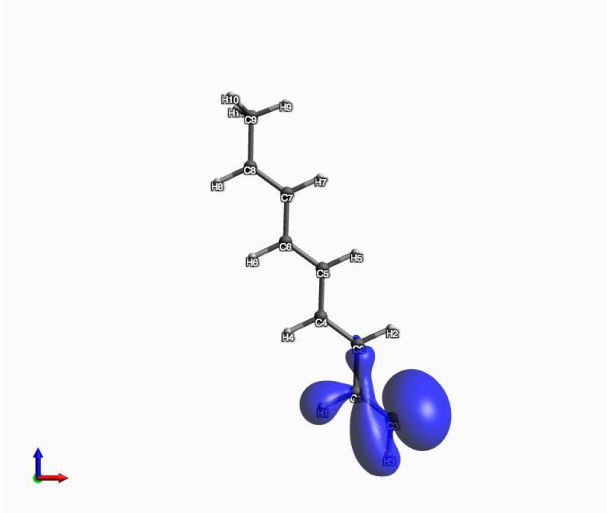
Right: the spin-density when π -TSP effect is switched off .

“Spin-delocalization” and “spin-polarization”

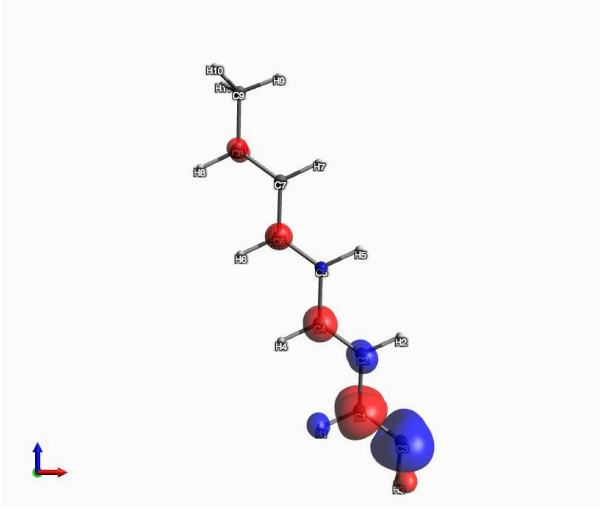
Definition: restricted versus unrestricted (for now) or something else?



Unrestricted spin-density
(Isosurface value =0.002)

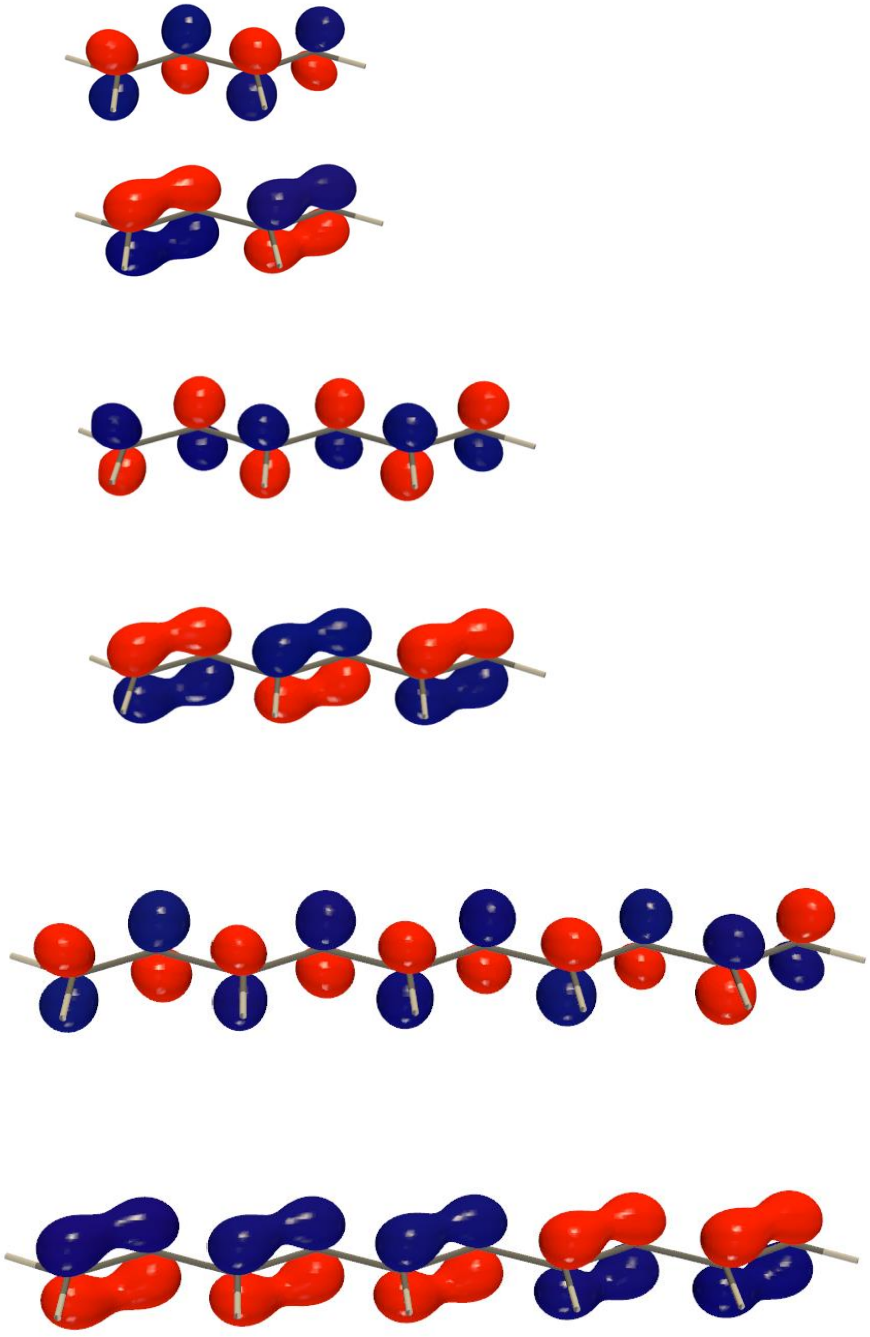


Restricted SOMO
(Isosurface value=0.002)



Difference
(Isosurface value=0.002)

HFCC(MHz)	C1	C2	C3	C4	C5	C6	C7	C8
UKS	429.10	4.02	45.93	-4.94	2.68	-2.04	1.79	-1.58
RKS	421.50	38.41	35.95	0.12	0.170	0.28	0.02	0.01
Diff.	7.6	-34.39	6.98	-5.06	2.51	-2.32	1.77	-1.59



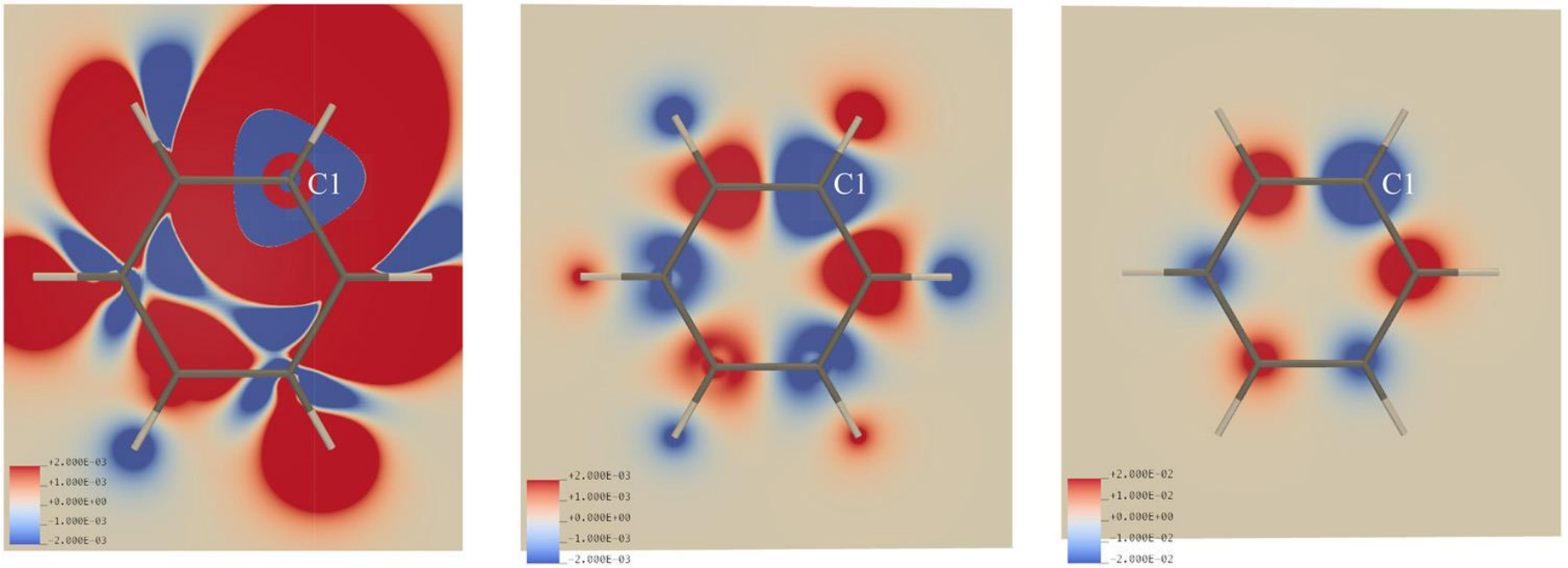


Fig. 5 The spin-density in benzene induced by FC(C1) (color-coded according to the density values, given in a.u.).

***Left**: the total spin-density (in the molecular plane).*
***Middle**: spin polarization only due to the π-TSP (in the molecular plane).*
***Right**: the spin-polarization of the group of π-orbitals is shown in the plane 0.5 Å below the molecular plane.*

CDD

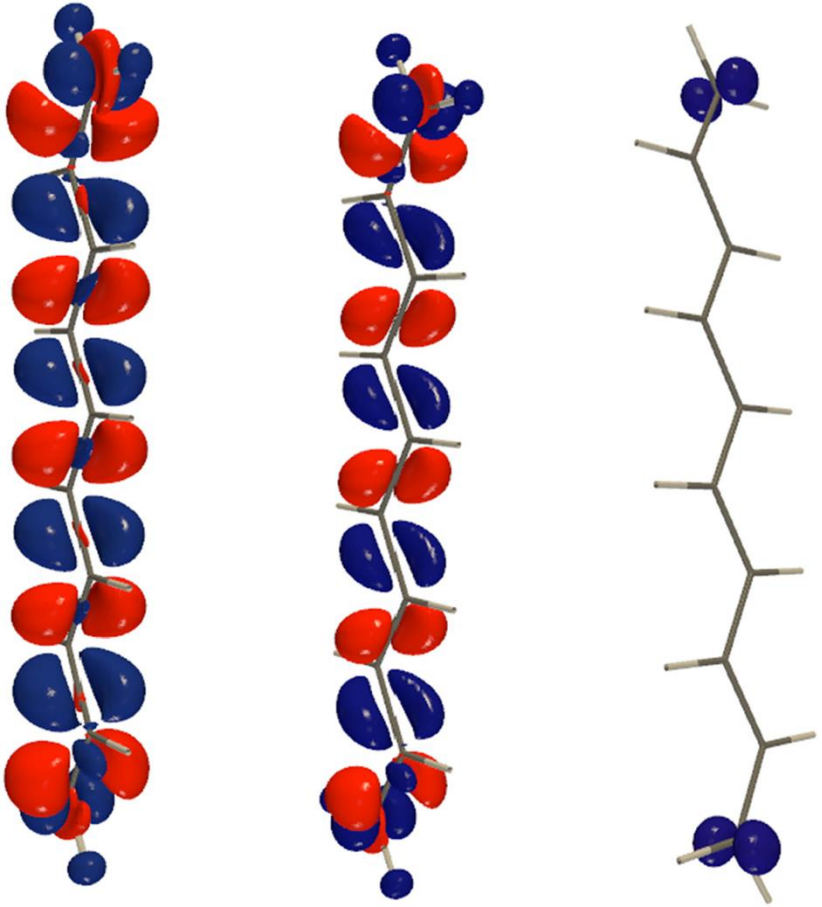


Fig. 8 CDD for ^{9}J(C1–C10) in 1,3,5,7,9-decapentaene:

Left: the total CDD
Middle: the CDD due to the π-TSP effect (middle)
Right: the CDD when the π-TSP effect is switched off

The isosurface value in all plots is 0.001 a.u.