

Electronic Supplementary Material

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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Table S1. Calculated nJ (C1- C_{n+1}) in 1,3,5,7,9-decapentaene in Hz calculated using the P86 exchange-correlation functional.

n	FC	PSO	DSO	SUM ^a
1	77.44	-8.60	0.14	68.98
2	1.86	0.16	-0.05	1.97
3	7.43	0.62	-0.08	7.97
4	-0.72	0.02	-0.04	-0.74
5	1.04	-0.11	-0.04	0.89
6	-0.70	0.02	-0.02	-0.70
7	0.73	0.05	-0.02	0.76
8	-0.54	0.01	-0.01	-0.54
9	0.52	0.01	-0.01	0.52

a) The calculation of the SD term is not implemented in the deMon program.

Table S2. Calculated nJ (C1- C_{n+1}) in benzene in Hz calculated using the P86 exchange-correlation functional.

n	FC	PSO	DSO	SUM ^a
2	62.94	-6.61	0.21	56.54
3	-0.33	0.04	-0.02	-0.31
4	7.80	0.46	-0.01	8.25

a) The calculation of the SD term is not implemented in the deMon program.

Table S3. Calculated ${}^nJ(\text{C1}-\text{C}_{n+1})$ in naphthalene in Hz calculated using the P86 exchange-correlation functional.

n		FC	PSO	DSO	SUM ^a
1	C1-C2	67.97	-7.46	0.22	60.73
	C1-C9	61.28	-5.38	0.28	56.18
	C2-C3	59.07	-5.43	0.22	53.86
	C9-C10	55.82	-5.45	0.33	50.7
2	C1-C8	3.78	-0.05	0.01	3.74
	C1-C10	1.14	-0.03	0.03	1.14
	C2-C9	0.36	-0.02	0.02	0.36
	C1-C3	-0.03	0.08	-0.01	0.04
3	C3-C9	6.45	0.21	0.03	6.69
	C1-C4	5.33	0.34	0.01	5.68
	C1-C5	2.35	-0.21	-0.06	2.08
4	C2-C7	0.52	0.05	-0.06	0.51
	C1-C6	-0.50	0.01	-0.06	-0.55
5	C2-C6	0.46	0.01	-0.05	0.42

a) The calculation of the SD term is not implemented in the deMon program

Table S4. ${}^nJ(\text{C1}-\text{C}_{n+1})$ in 1,3,5,7,9-decapentaene in Hz calculated^a using the BP86 and B3LYP exchange-correlation functionals.

n	V_{xc}	FC	SD	PSO	DSO	Total
1	BP86	70.88	3.01	-8.56	0.14	65.47
	B3LYP	83.76	4.69	-9.18	0.13	79.41
2	BP86	2.44	-1.85	0.17	-0.05	0.70
	B3LYP	-0.90	-4.00	0.17	-0.05	-4.78
3	BP86	6.92	2.64	0.65	-0.08	10.12
	B3LYP	9.77	4.53	0.66	-0.08	14.88
4	BP86	-0.37	-1.11	0.02	-0.04	-1.51
	B3LYP	-2.83	-2.84	0.02	-0.04	-5.69
5	BP86	0.68	1.79	-0.11	-0.04	2.32
	B3LYP	2.99	3.61	-0.11	-0.04	6.46
6	BP86	-0.48	-0.65	0.02	-0.02	-1.14
	B3LYP	-2.38	-1.89	0.02	-0.02	-4.28
7	BP86	0.45	1.47	0.05	-0.02	1.95
	B3LYP	2.26	3.06	0.05	-0.02	5.35
8	BP86	-0.39	-0.37	0.01	-0.01	-0.77
	B3LYP	-1.70	-1.06	0.01	-0.01	-2.77
9	BP86	0.30	1.18	0.00	-0.01	1.46
	B3LYP	1.56	2.39	0.01	-0.01	3.94

a) IGLO-II basis set (ref. 1), G03 package (ref. 21).

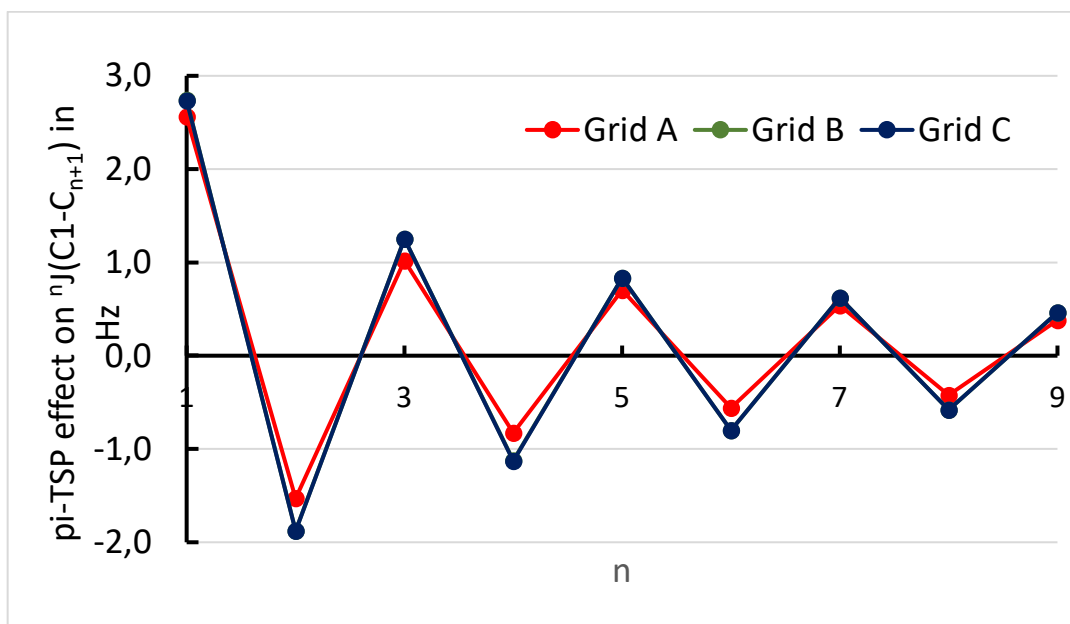


Figure S1. The π -TSP effect on ${}^nJ^{\text{FC}}(\text{C1}-\text{C}_{n+1})$ in 1,3,5,7,9-decapentaene as a function of the number of bonds separating two carbons (in Hz) calculated using three different grids for numerical integration. Grid A: about 3000 points/atom during the main SCF procedure, then an extra SCF iteration with about 10500 points/atom; Grid B: about 10500 points/atom; Grid C: about 20000 points/atom.

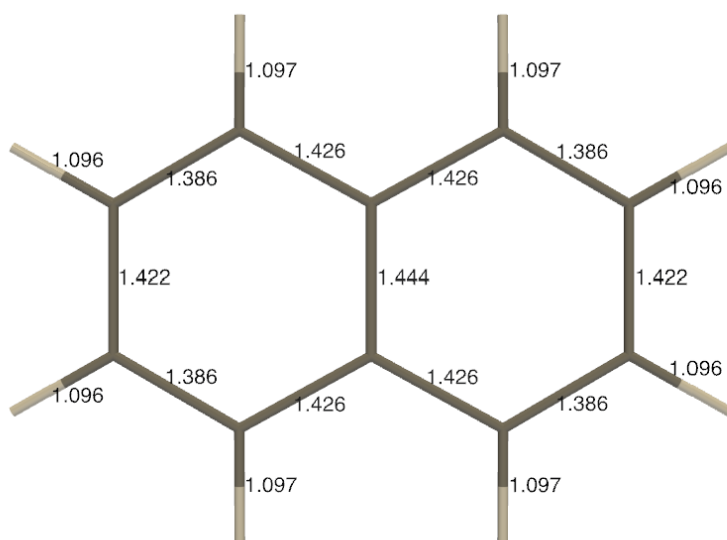


Figure S2. The bond lengths in the optimized structure of naphthalene.

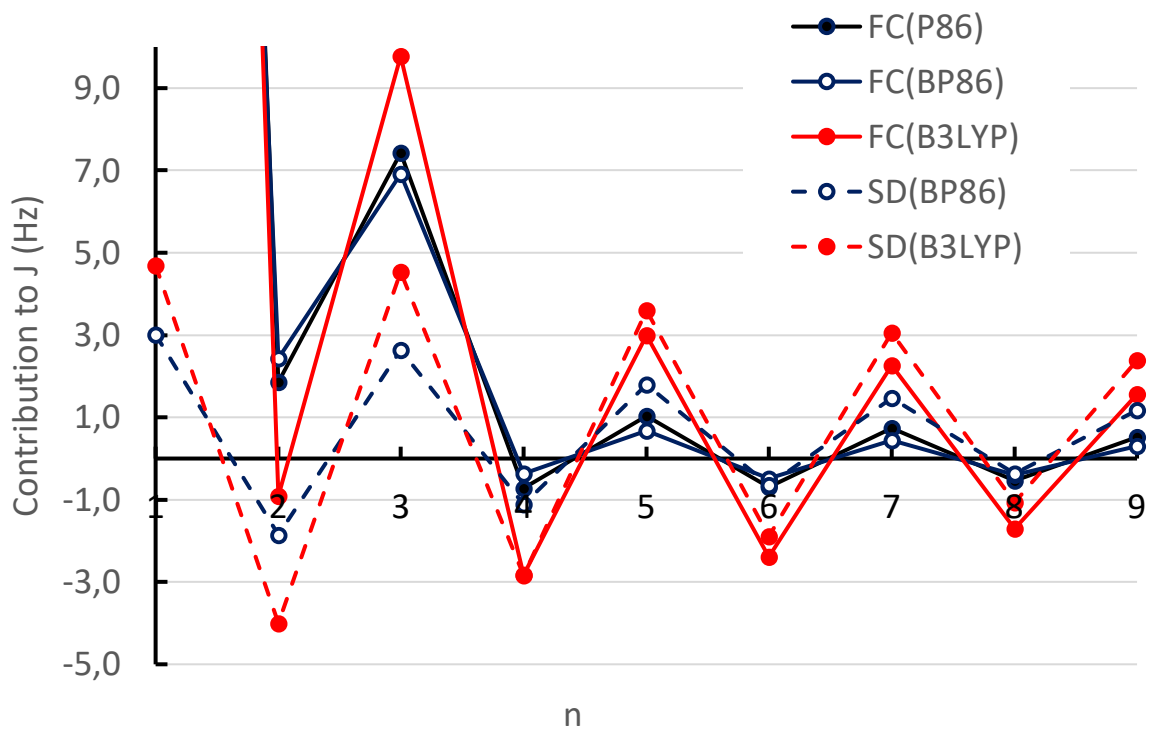


Figure S3. The FC and SD contributions to nJ (C_1-C_{n+1}) in 1,3,5,7,9-decapentaene calculated with different exchange-correlation functionals. The B3LYP and BP86 results were obtained using the G03 package (ref. 21).

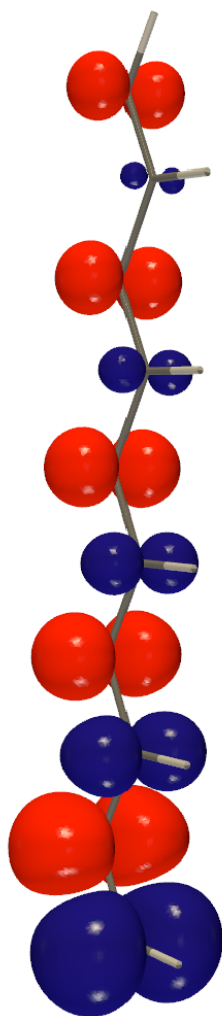


Figure S4. Spin-polarization of π -orbitals taken together in 1,3,5,7,9-decapentaene due to FC(C1). The isosurface value is 0.007 a.u.

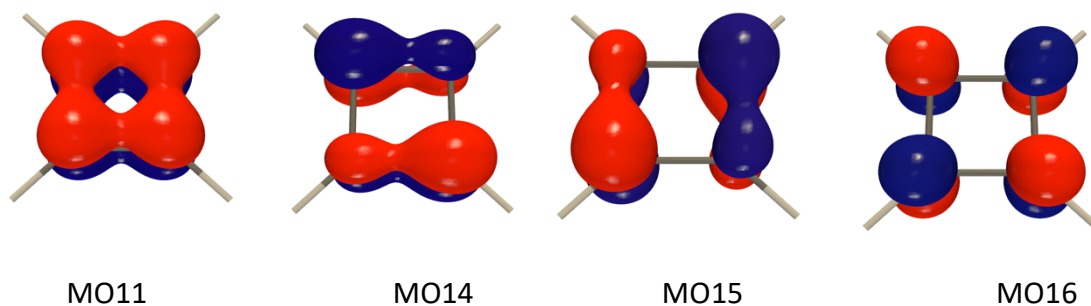


Figure S5. The occupied π -orbital (MO11) and the lowest vacant π -orbitals (MO14, MO15 and MO16) of a cyclobutadienyl dication. The isosurface value 0.1 a.u. .

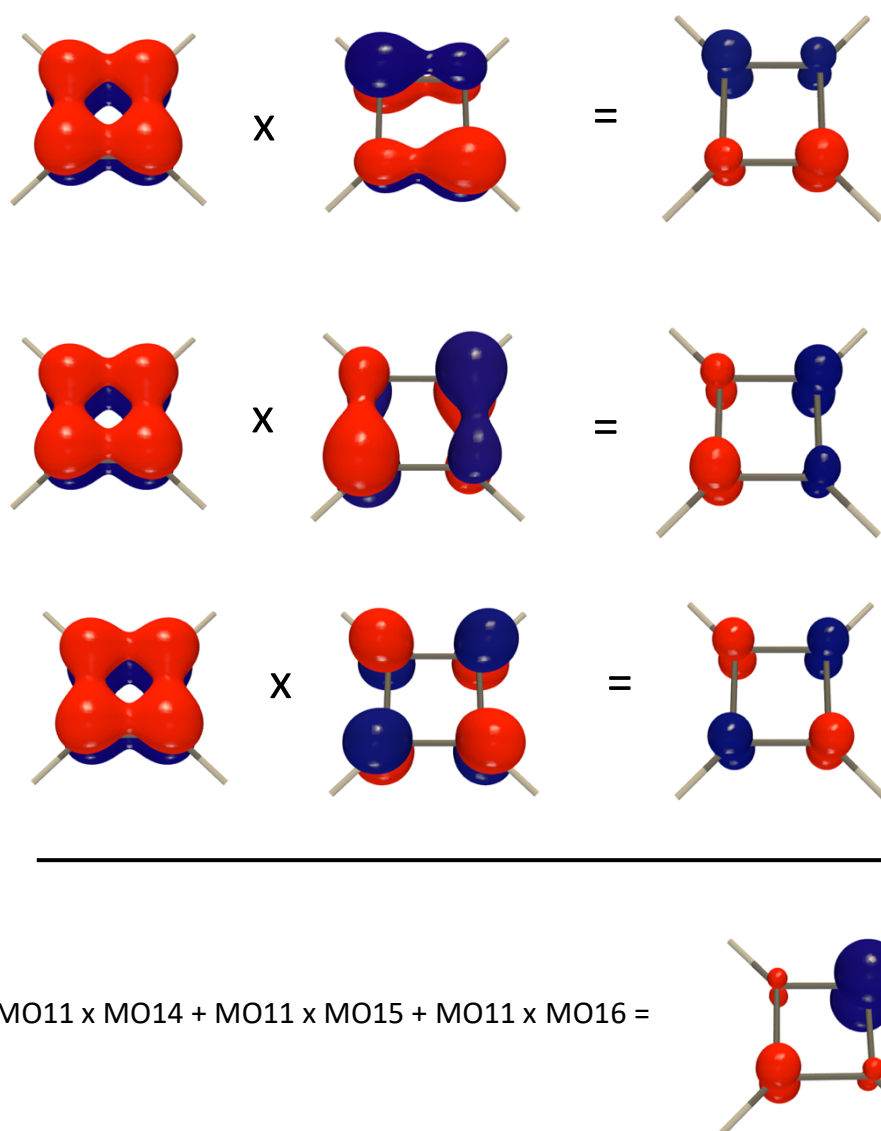


Figure S6. The contributions of the products of the occupied π -orbital with low-lying vacant π -orbitals to the spin-density induced by FC(C1) in a cyclobutadienyl dication. The isosurface value is 0.1 a.u. for MOs and 0.02 a.u. for their products.

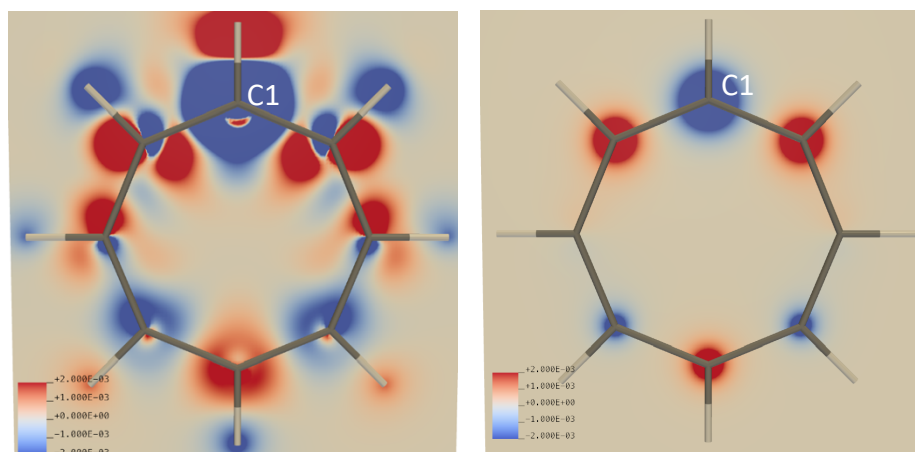


Figure S7. The π -TSP effect on the spin density in a cyclooctatetranyl dication induced by FC(C1) (left; color-coded according to the density values given in a.u.) in the dication plane and the total spin-polarization of the π -orbitals in the plane 0.5 Å below the molecular plane; right).

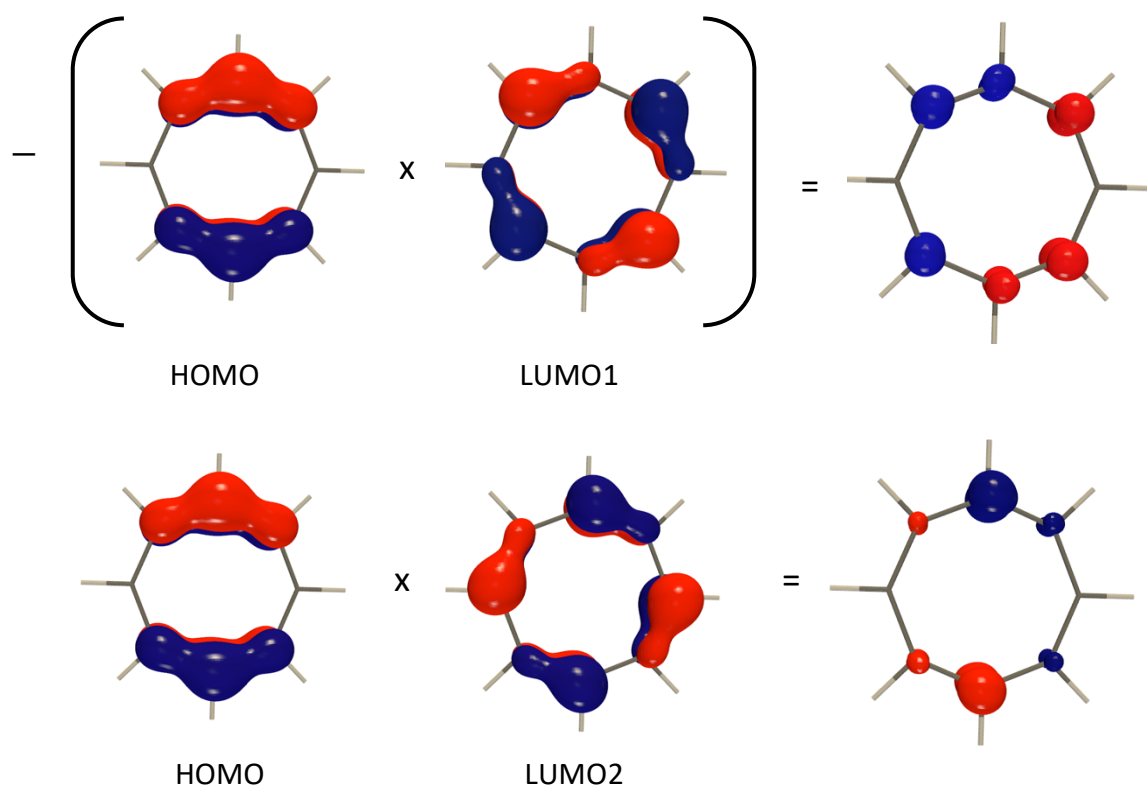


Figure S8. The products of the HOMO and LUMO orbitals for a cyclooctatetranyl dication. The first product is taken with a negative sign because the corresponding coefficient τ is negative (see Eqs. 2-4 in the main text). The isosurface value is 0.07 a.u. for MOs and 0.01 a.u for their products.

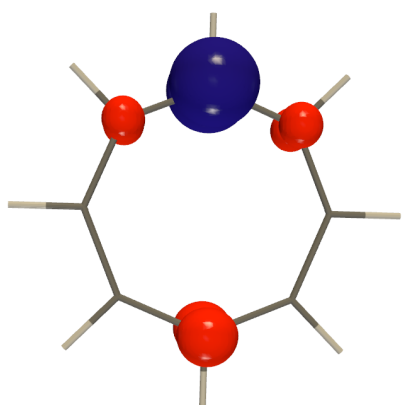


Figure S9. The overall contribution of the HOMO to the spin density induced by FC(C1) in a cyclooctatetraenyl dication (compare with Figure S5, left). The isosurface value is 0.01.

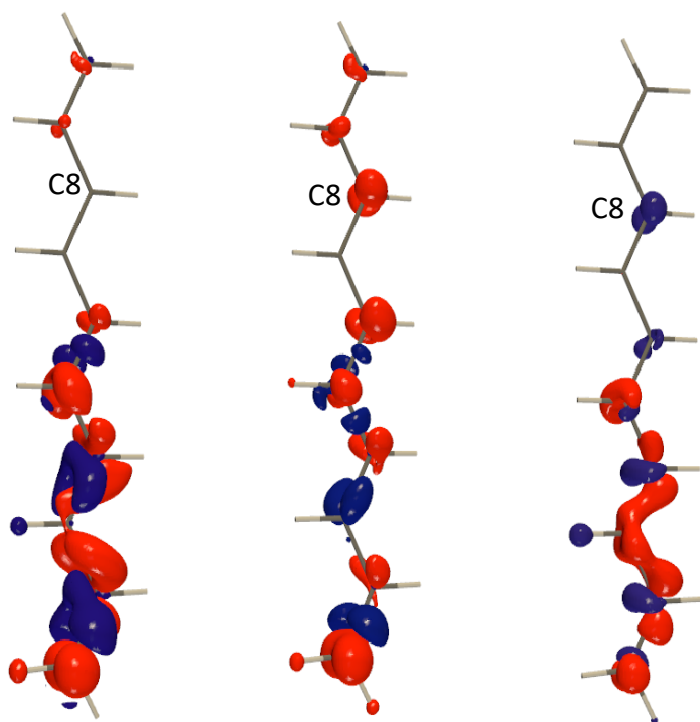


Figure S10. The CDD for ${}^4J(\text{C1-C5})$ in 1,3,5,7,9-decapentaene: total (left), due the π -TSP effect (middle) and the CDD when the π -TSP effect is switched off (right). The isosurface value in all plots is 0.004 a.u.

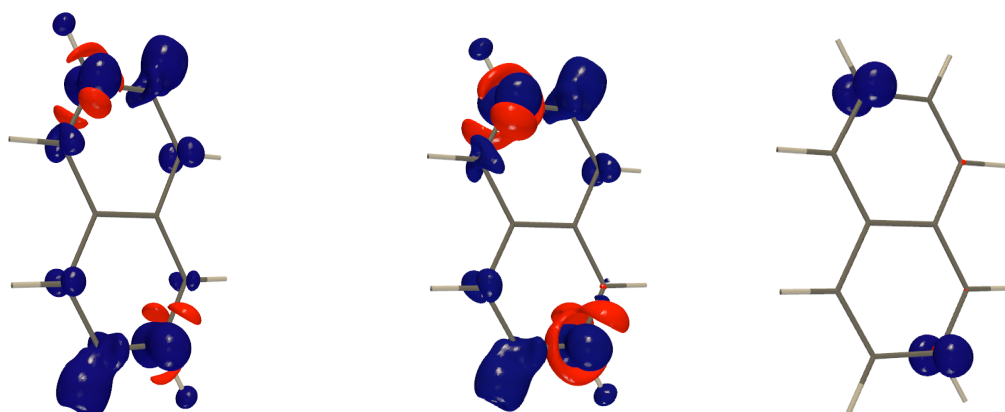


Figure S11. CDD for ${}^5J(\text{C2-C6})$ in naphthalene: total (left), due the π -TSP effect (middle) and the CDD when the π -TSP effect is switched off (right). The isosurface value in all plots is 0.001 a.u.

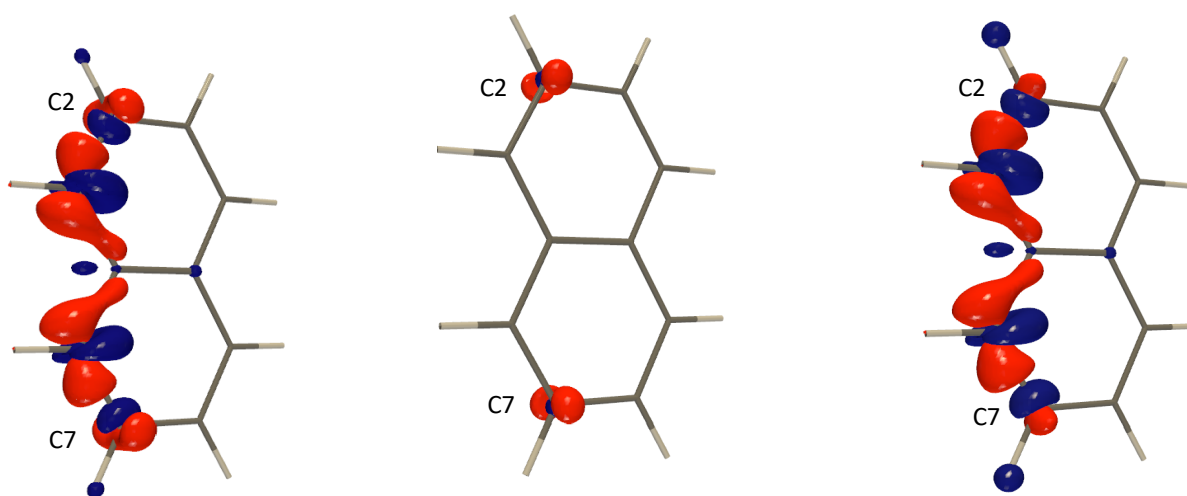


Figure S12. CDD for ${}^4J(\text{C2-C7})$ in naphthalene: total (left), due the π -TSP effect (middle) and the CDD when the π -TSP effect is switched off (right). The isosurface value in all plots is 0.004 a.u.

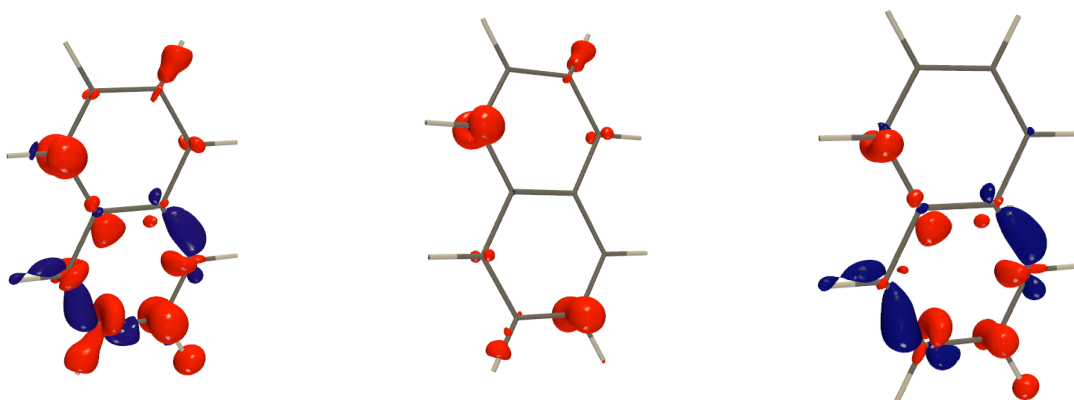


Figure S13. CDD for ${}^4J(\text{C1-C6})$ in naphthalene: total (left) due the π -TSP effect (middle) and the CDD when the π -TSP effect is switched off (right). The isosurface value in all plots is 0.002 a.u.

Table S5. The π -TSP effect on ${}^{13}\text{C}$ HFCC in the 1,3,5,7,9-decapentaene-1-yl radical for the optimized structure. The values are given in MHz.

Carbon	π -TSP ON	π -TSP OFF	Difference
1	337.30	322.82	14.48
2	-3.31	2.39	-5.70
3	87.76	87.36	0.40
4	0.33	4.74	-4.41
5	5.73	2.65	3.07
6	-2.15	0.64	-2.79
7	2.72	0.01	2.71
8	-2.30	-1.05	-1.25
9	1.84	0.25	1.58
10	-1.73	-1.65	-0.08

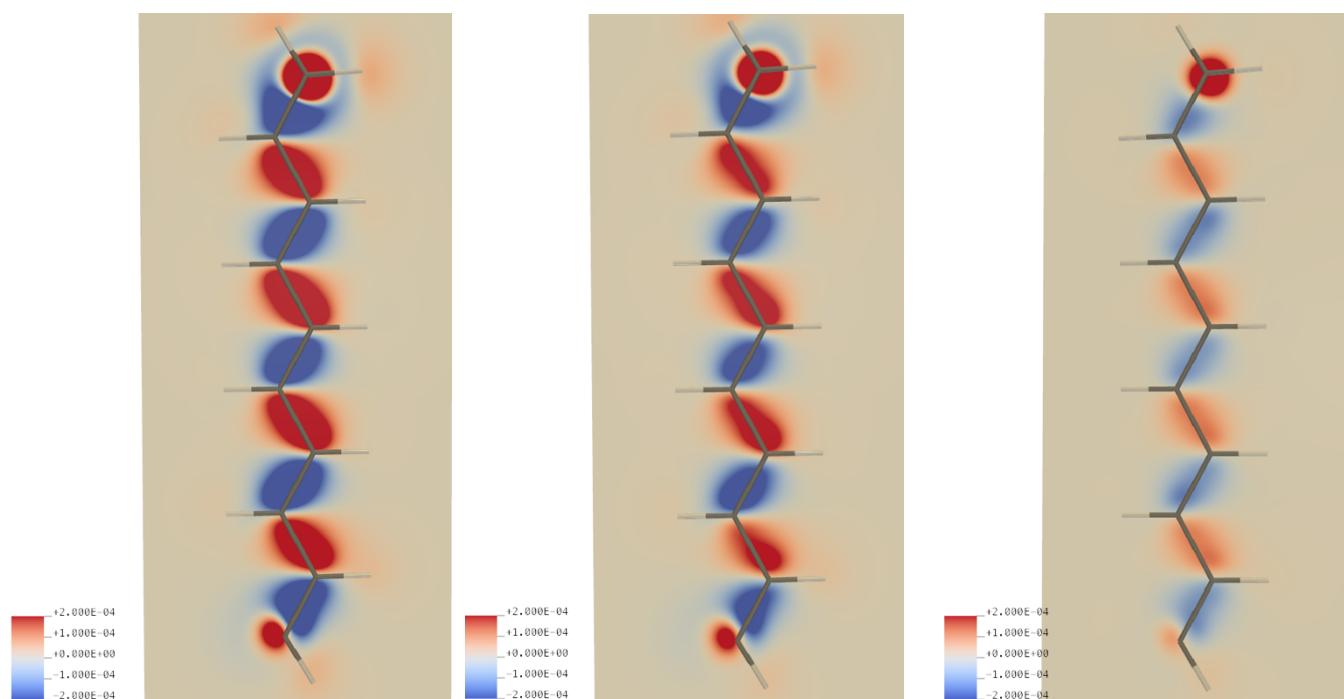


Figure S14. The C10 HFDD in the 1,3,5,7,9-decapentaen-1-yl radical (a); the π -TSP effect on the C10 HFDD (b) and the C10 HFDD when the π -TSP effect is switched off (c and d). The plots show HFDDs in the plane 0.5 Å below the radical plane.

Cartesian coordinates of the optimized structures used in this work (in Å):

1,3,5,7,9-decapentaene

C	5.57155652	0.22658449	0.00000000
C	4.36600585	-0.39674599	0.00000000
C	3.09207900	0.28462510	0.00000000
C	1.87752333	-0.35288057	0.00000000
C	0.60895764	0.31650229	0.00000000
C	-0.60666635	-0.32524946	0.00000000
C	-1.87524579	0.34410891	0.00000000
C	-3.08975700	-0.29350101	0.00000000
C	-4.36380817	0.38766895	0.00000000
C	-5.56925882	-0.23586894	0.00000000
H	6.51054405	-0.33548276	0.00000000
H	4.33296253	-1.49643498	0.00000000
H	3.11286760	1.38489525	0.00000000
H	1.86263989	-1.45364347	0.00000000
H	0.62183181	1.41703940	0.00000000
H	-0.61953786	-1.42578655	0.00000000
H	-1.86041124	1.44487033	0.00000000
H	-3.11035372	-1.39377864	0.00000000
H	5.64918963	1.32065942	0.00000000
H	-4.33100048	1.48735752	0.00000000

H	-5.64674361	-1.32995336	0.00000000
H	-6.50835102	0.32600995	0.00000000

Benzene

C	1.21636673	0.70226966	0.00000000
C	0.00000000	1.40453931	0.00000000
C	-1.21636673	0.70226966	0.00000000
C	-1.21636673	-0.70226966	0.00000000
C	0.00000000	-1.40453931	0.00000000
C	1.21636673	-0.70226966	0.00000000
H	2.16549152	1.25024712	0.00000000
H	0.00000000	2.50049422	0.00000000
H	-2.16549152	1.25024711	0.00000000
H	-2.16549152	-1.25024712	0.00000000
H	0.00000000	-2.50049422	0.00000000
H	2.16549152	-1.25024711	0.00000000

Naphthalene

C	-1.24872214	1.41037019	0.00000000
C	-2.44596401	0.71120114	0.00000000
C	-2.44596401	-0.71120114	0.00000000
C	-1.24872214	-1.41037019	0.00000000
C	1.24872214	-1.41037019	0.00000000
C	2.44596401	-0.71120114	0.00000000
C	2.44596401	0.71120114	0.00000000
C	1.24872214	1.41037019	0.00000000
C	0.00000000	0.72204322	0.00000000
C	0.00000000	-0.72204322	0.00000000
H	-1.24451964	2.50721371	0.00000000
H	-3.39819664	1.25308018	0.00000000
H	-3.39819664	-1.25308018	0.00000000
H	-1.24451964	-2.50721371	0.00000000
H	1.24451964	-2.50721371	0.00000000
H	3.39819664	-1.25308018	0.00000000
H	3.39819664	1.25308018	0.00000000
H	1.24451964	2.50721371	0.00000000

1,3,5,7,9-decapentaen-1-yl radical

C	-2.40149636	-5.01194437	0.00000000
C	-2.36081202	-3.67617444	0.00000000
C	-1.15104000	-2.86688171	0.00000000
C	-1.15759986	-1.49581841	0.00000000
C	0.02317277	-0.68074443	0.00000000
C	0.01494579	0.69367383	0.00000000
C	1.19470635	1.50971314	0.00000000

C	1.18921531	2.88132298	0.00000000
C	2.38146967	3.69733141	0.00000000
C	2.38341658	5.05445237	0.00000000
H	-3.31264099	-3.11772101	0.00000000
H	-0.18930342	-3.39833737	0.00000000
H	-2.12723114	-0.97493033	0.00000000
H	0.99313506	-1.20066202	0.00000000
H	-0.95523966	1.21331677	0.00000000
H	2.16430738	0.98846773	0.00000000
H	0.22257379	3.40725204	0.00000000
H	-1.68561535	-5.83685490	0.00000000
H	3.34204371	3.16095891	0.00000000
H	1.44789566	5.62698300	0.00000000
H	3.31468574	5.62919382	0.00000000

Cyclobutadienyl dication

C	0.72997582	0.72997582	0.00000000
C	-0.72997582	0.72997582	0.00000000
C	0.72997582	-0.72997582	0.00000000
C	-0.72997582	-0.72997582	0.00000000
H	1.51268973	1.51268973	0.00000000
H	-1.51268973	1.51268973	0.00000000
H	1.51268973	-1.51268973	0.00000000
H	-1.51268973	-1.51268973	0.00000000

Cyclooctatetranyl dication

C	1.85403202	0.00000045	0.00000000
C	1.31099830	-1.31099894	0.00000000
C	0.00000045	-1.85403202	0.00000000
C	-1.31099894	-1.31099830	0.00000000
C	-1.85403202	-0.00000045	0.00000000
C	-1.31099830	1.31099894	0.00000000
C	-0.00000045	1.85403202	0.00000000
C	1.31099894	1.31099830	0.00000000
H	2.95368374	0.00001701	0.00000000
H	2.08855777	-2.08858182	0.00000000
H	0.00001701	-2.95368374	0.00000000
H	-2.08858182	-2.08855777	0.00000000
H	-2.95368374	-0.00001701	0.00000000
H	-2.08855777	2.08858182	0.00000000
H	-0.00001701	2.95368374	0.00000000
H	2.08858182	2.08855777	0.00000000