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The Effect of the Two Types of Dibenzoannulation of Pentalene on Molecular Energies and Magnetically Induced Currents

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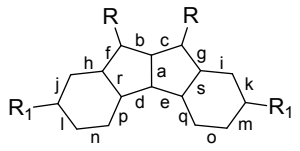
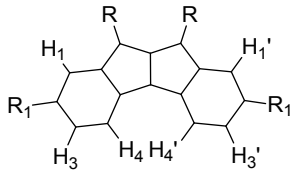
Table S1. Experimentally observed and calculated bond lengths of dibenzo[*a*,*f*]pentalene.



R = Mes, R_1 = Me[a]			R = R_1 = H[b]				
molecule A		molecule B	C_s open-shell singlet	C_s closed-shell singlet	C_{2v} open-shell singlet	C_{2v} closed-shell singlet	C_{2v} triplet
a	1.457(3)	1.458(2)	1.455	1.451	1.421	1.420	1.458
b	1.434(3)	1.428(3)	1.446	1.454	1.418	1.418	1.403
c	1.408(3)	1.415(3)	1.370	1.367	1.418	1.418	1.403
d	1.404(3)	1.414(3)	1.390	1.378	1.430	1.424	1.434
e	1.428(3)	1.419(3)	1.453	1.461	1.430	1.424	1.434
f	1.425(3)	1.435(3)	1.393	1.376	1.423	1.412	1.451
g	1.451(3)	1.441(2)	1.465	1.468	1.423	1.412	1.451
h	1.412(3)	1.408(3)	1.423	1.433	1.404	1.409	1.392
i	1.396(3)	1.403(3)	1.385	1.384	1.404	1.409	1.392
j	1.378(3)	1.382(3)	1.372	1.352	1.388	1.382	1.401
k	1.390(3)	1.386(2)	1.406	1.407	1.388	1.382	1.401
l	1.421(3)	1.422(3)	1.433	1.445	1.409	1.415	1.398
m	1.402(3)	1.420(3)	1.391	1.389	1.409	1.415	1.398
n	1.371(3)	1.379(3)	1.373	1.364	1.393	1.389	1.399
o	1.385(3)	1.377(3)	1.407	1.410	1.393	1.389	1.399
p	1.411(3)	1.409(3)	1.421	1.430	1.399	1.403	1.395
q	1.397(3)	1.402(2)	1.387	1.384	1.399	1.403	1.395
r	1.460(3)	1.451(2)	1.483	1.497	1.457	1.465	1.444
s	1.450(3)	1.454(3)	1.436	1.434	1.457	1.465	1.444

[a] Experimentally obtained by X-ray analysis. Data are for the two crystallographically independent molecules (A and B), taken from ref. 16 in the manuscript. [b] Calculated at the (U)B3LYP/6-311+G(d,p) level of theory (this work).

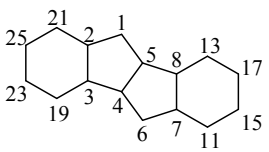
Table S2. Experimentally observed and calculated ^{1}H NMR chemical shifts of dibenzo[*a*,*f*]pentalene (ppm) relative to TMS.

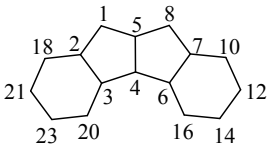


	R = Mes, R_1 = Me[a]	R = Mes, R_1 = H[a]	R = R_1 = H[b]	
			C_s open-shell singlet H/H'/av[c]	C_s closed-shell singlet H/H'/av[c]
H_1	4.49	4.53	4.90/4.48/4.69	4.72/4.12/4.42
H_2 (R_1 = H)	/	5.09-5.13	4.99/4.46/4.73	4.81/3.94/4.37
H_3	5.33	5.40	5.23/4.64/4.94	5.15/4.26/4.71
H_4	5.20	5.09-5.13	4.45/4.23/4.34	4.10/3.69/3.90

[a] Experimental data taken from ref. 16 in the manuscript. [b] Calculated at the (U)B3LYP/6-311+G(d,p) level of theory (this work). [c] Average values.

Table S3. Spin densities in dibenzopentalenes obtained by Hirshfeld[1] population analysis.





[*a*,*e*]-DBP	triplet	**[*a*,*f*]-DBP**	singlet	triplet
C1	0.23	C1	0.00	0.36
C2	0.14	C2	-0.03	0.07
C3	0.14	C3	0.02	0.06
C4	0.17	C4	-0.17	0.33
C5	0.17	C5	-0.02	0.02
C6	0.23	C6	0.06	0.06
C7	0.14	C7	-0.06	0.07
C8	0.14	C8	0.24	0.36
H9	0.01	H9	0.02	0.02
H10	0.01	C10	0.08	0.06
C11	0.03	H11	0.01	0.00
H12	0.00	C12	-0.09	0.09
C13	0.04	H13	-0.01	0.01
H14	0.00	C14	0.08	0.06
C15	0.12	H15	0.01	0.00
H16	0.01	C16	-0.07	0.08
C17	0.10	H17	0.00	0.00
H18	0.01	C18	0.02	0.06
C19	0.04	H19	0.00	0.00
H20	0.00	C20	-0.05	0.08
C21	0.03	C21	-0.04	0.09
H22	0.00	H22	0.00	0.01
C23	0.10	C23	0.03	0.06
H24	0.01	H24	0.00	0.00
C25	0.12	H25	0.00	0.02
H26	0.01	H26	0.00	0.00
Tot	2.00	Tot	0.00	2.00

[1] F. L. Hirshfeld, *Theor. Chim. Acta.* **1977**, *44*, 129-138.

S1: Additional examination of factors responsible for energy lowering upon closed-shell to open-shell singlet transition of dibenzo[*a*,*f*]pentalene

The closed-shell/open-shell singlet transition mainly involves changes of the *ortho*-quinodimethane subunit (Figure S1A). In the performed energy decomposition scheme closed-shell and open-shell dibenzo[*a*,*f*]pentalene species were formed from fragments **C** and **D**, which should form two σ and two π bonds in the closed-shell species and are, thus, taken in their quintet electronic state (Figure S1B). If open-shell species is to be formed, the two fragments should change their electronic state, which is also accompanied by geometry changes. For the [*a*,*f*]-DBP_{os} to be formed, the two fragments can have open-shell singlet states or triplet states (Figure S1C). The results of the analyses are shown in Table S4.

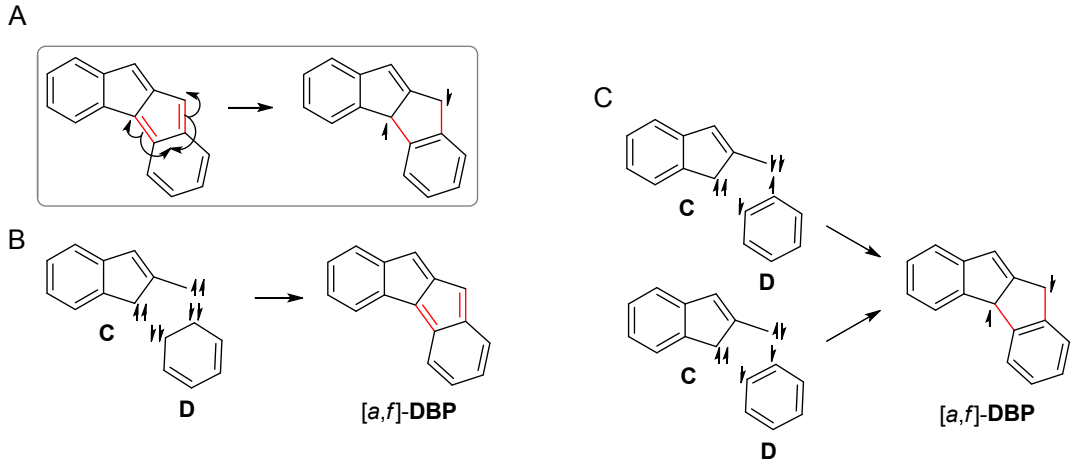


Figure S1. Transition from closed-shell to open-shell dibenzo[*a*,*f*]-pentalene (A), formation of the closed-shell [*a*,*f*]-DBP (B) and open-shell [*a*,*f*]-DBP (C) from fragments **C** and **D**.

The two analyses are consistent with one another and also with the results described in the manuscript. As the data in Table S4 show, the slight energy lowering comes exclusively from deformation energy component, which should be related to benzene subunit formation that drives the molecule toward singlet diradical. The large and negative $\Delta E_{def} = -56.35$ kcal/mol and $\Delta E_{def} = -57.44$ kcal/mol for [*a*,*f*]-DBP_{os} are also reflections of benzene formation within fragment **D**.

Table S4. Contribution of various energy components to the total binding interactions between fragments **C** and **D** in dibenzo[*a*,*f*]pentalene in its closed-shell and open-shell singlet states and energy changes (values in bold) upon closed-shell → open-shell transition.[a] Values are in kcal/mol, calculated at the UB3LYP/6-311+G(d,p) level.

Molecule	ΔE_{tot} **ΔE**	ΔE_{def} **$\Delta\Delta E_{def}$**	ΔE_{int} **$\Delta\Delta E_{int}$**	ΔE_{elstat} **$\Delta\Delta E_{elstat}$**	ΔE_{Pauli} **$\Delta\Delta E_{Pauli}$**	ΔE_{oi} **$\Delta\Delta E_{oi}$**	ΔE_{disp} **$\Delta\Delta E_{disp}$**	Interacting fragments[b]
[*a*,*f*]-**DBP**$_{cs}$	-312.91	17.95	-330.86	-360.16	575.28	-473.34	-72.64	**C**(quin) + **D**(quin)
[*a*,*f*]-**DBP**$_{os}$	-313.23	-56.35	-256.88	-436.33	979.44	-755.43	-44.56	**C**(s os) + **D**(s os)
[*a*,*f*]-**DBP**$_{os}$	-313.24	-57.44	-255.80	-467.42	967.79	-708.69	-47.48	**C**(t) + **D**(t)
[*a*,*f*]$_{cs}$ → [*a*,*f*]$_{os}$	**-0.32**	**-74.30**	**73.98**	**-76.17**	**404.16**	**-282.09**	**28.08**	
[*a*,*f*]$_{cs}$ → [*a*,*f*]$_{os}$	**-0.32**	**-75.38**	**75.06**	**-107.26**	**392.51**	**-235.35**	**25.16**	

[a] ΔE_{tot} = total binding energy between two fragments, ΔE_{def} = deformation energy, ΔE_{int} = interaction energy, ΔE_{elstat} = electrostatic energy, ΔE_{Pauli} = Pauli repulsion, ΔE_{oi} = orbital interaction energy, ΔE_{disp} = dispersion energy, ΔE_{iso} = isomerization energy. [b]quin = quintet, s os = open-shell singlet, t = triplet.

Absolute energies and x, y, z coordinates of optimized structures

[*a*,*e*]-DBP singlet
E = –615.8507052 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.559843	0.783586	0.000000
2	6	0	-0.780613	2.037779	0.000000
3	6	0	0.609874	1.717755	0.000000
4	6	0	0.689487	0.255812	0.000000
5	6	0	-0.689487	-0.255812	0.000000
6	6	0	1.559843	-0.783586	0.000000
7	6	0	0.780613	-2.037779	0.000000
8	6	0	-0.609874	-1.717755	0.000000
9	1	0	-2.641601	0.741514	0.000000
10	1	0	2.641601	-0.741514	0.000000
11	6	0	1.195472	-3.360979	0.000000
12	1	0	2.250370	-3.613930	0.000000
13	6	0	-1.559843	-2.724914	0.000000
14	1	0	-2.619198	-2.492756	0.000000
15	6	0	0.224977	-4.375415	0.000000
16	1	0	0.536314	-5.413867	0.000000
17	6	0	-1.131188	-4.062475	0.000000
18	1	0	-1.866201	-4.859336	0.000000
19	6	0	1.559843	2.724914	0.000000
20	1	0	2.619198	2.492756	0.000000
21	6	0	-1.195472	3.360979	0.000000
22	1	0	-2.250370	3.613930	0.000000
23	6	0	1.131188	4.062475	0.000000
24	1	0	1.866201	4.859336	0.000000
25	6	0	-0.224977	4.375415	0.000000
26	1	0	-0.536314	5.413867	0.000000

[*a*,*e*]-DBP triplet

E = –615.7992303 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.592178	0.823323	0.000000
2	6	0	-0.810862	2.010486	0.000000
3	6	0	0.616780	1.664858	0.000000
4	6	0	0.692893	0.257989	0.000000
5	6	0	-0.692893	-0.257989	0.000000
6	6	0	1.592178	-0.823323	0.000000
7	6	0	0.810862	-2.010486	0.000000
8	6	0	-0.616780	-1.664858	0.000000
9	1	0	-2.671821	0.783804	0.000000
10	1	0	2.671821	-0.783804	0.000000
11	6	0	1.184689	-3.370249	0.000000
12	1	0	2.232324	-3.650663	0.000000
13	6	0	-1.591062	-2.685667	0.000000
14	1	0	-2.645673	-2.433243	0.000000
15	6	0	0.201134	-4.338580	0.000000
16	1	0	0.482625	-5.385977	0.000000
17	6	0	-1.184689	-4.002006	0.000000
18	1	0	-1.919672	-4.798375	0.000000
19	6	0	1.591062	2.685667	0.000000
20	1	0	2.645673	2.433243	0.000000
21	6	0	-1.184689	3.370249	0.000000
22	1	0	-2.232324	3.650663	0.000000
23	6	0	1.184689	4.002006	0.000000
24	1	0	1.919672	4.798375	0.000000
25	6	0	-0.201134	4.338580	0.000000
26	1	0	-0.482625	5.385977	0.000000

[*a*,*f*]-DBP singlet

E = –615.8161769 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.652374	1.673119	0.000000
2	6	0	-2.297194	0.354070	0.000000
3	6	0	-1.272246	-0.648955	0.000000
4	6	0	0.000000	0.069797	0.000000
5	6	0	-0.297697	1.489964	0.000000
6	6	0	1.370554	-0.070761	0.000000
7	6	0	1.960190	1.304709	0.000000
8	6	0	0.949336	2.238590	0.000000
9	1	0	1.060566	3.313405	0.000000
10	6	0	3.385232	1.454372	0.000000
11	1	0	3.821274	2.447713	0.000000
12	6	0	4.173607	0.344300	0.000000
13	1	0	5.253172	0.441760	0.000000
14	6	0	3.601504	-0.983043	0.000000
15	1	0	4.277155	-1.831674	0.000000
16	6	0	2.253863	-1.195093	0.000000
17	1	0	1.854030	-2.202521	0.000000
18	6	0	-3.637311	0.008463	0.000000
19	1	0	-4.407950	0.772326	0.000000
20	6	0	-1.630566	-1.985502	0.000000
21	6	0	-3.988291	-1.354242	0.000000
22	1	0	-5.032716	-1.642627	0.000000
23	6	0	-2.998180	-2.328127	0.000000
24	1	0	-3.279519	-3.375541	0.000000
25	1	0	-2.188492	2.614782	0.000000
26	1	0	-0.880080	-2.767601	0.000000

[*a*,*f*]-DBP singlet open-shell

E = –615.8165968 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.536128	1.797768	0.000000
2	6	0	-2.266197	0.527113	0.000000
3	6	0	-1.312289	-0.546807	0.000000
4	6	0	0.000000	0.077785	0.000000
5	6	0	-0.194336	1.519925	0.000000
6	6	0	1.368779	-0.166970	0.000000
7	6	0	2.050114	1.150228	0.000000
8	6	0	1.098679	2.167565	0.000000
9	1	0	1.294066	3.230277	0.000000
10	6	0	3.471870	1.197875	0.000000
11	1	0	3.981242	2.155577	0.000000
12	6	0	4.183989	0.025708	0.000000
13	1	0	5.267759	0.049869	0.000000
14	6	0	3.523652	-1.246283	0.000000
15	1	0	4.130240	-2.145261	0.000000
16	6	0	2.154796	-1.350714	0.000000
17	1	0	1.677689	-2.323929	0.000000
18	6	0	-3.627090	0.267307	0.000000
19	1	0	-4.347277	1.078814	0.000000
20	6	0	-1.759088	-1.859361	0.000000
21	6	0	-4.065415	-1.068677	0.000000
22	1	0	-5.126991	-1.286518	0.000000
23	6	0	-3.143701	-2.110500	0.000000
24	1	0	-3.496236	-3.135942	0.000000
25	1	0	-2.005730	2.773647	0.000000
26	1	0	-1.060589	-2.688313	0.000000

[*a*,*f*]-DBP triplet

E = –615.8164253 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	1.328627	2.014669
2	6	0	0.000000	2.183502	0.842246
3	6	0	0.000000	1.361568	-0.344691
4	6	0	0.000000	0.000000	0.106256
5	6	0	0.000000	0.000000	1.563961
6	6	0	0.000000	-1.361568	-0.344691
7	6	0	0.000000	-2.183502	0.842246
8	6	0	0.000000	-1.328627	2.014669
9	1	0	0.000000	-1.676130	3.038345
10	6	0	0.000000	-3.569828	0.721956
11	1	0	0.000000	-4.201576	1.603628
12	6	0	0.000000	-4.143738	-0.555854
13	1	0	0.000000	-5.223448	-0.655307
14	6	0	0.000000	-3.348198	-1.705559
15	1	0	0.000000	-3.818102	-2.682213
16	6	0	0.000000	-1.953028	-1.607708
17	1	0	0.000000	-1.345453	-2.505463
18	6	0	0.000000	3.569828	0.721956
19	1	0	0.000000	4.201576	1.603628
20	6	0	0.000000	1.953028	-1.607708
21	6	0	0.000000	4.143738	-0.555854
22	1	0	0.000000	5.223448	-0.655307
23	6	0	0.000000	3.348198	-1.705559
24	1	0	0.000000	3.818102	-2.682213
25	1	0	0.000000	1.676130	3.038345
26	1	0	0.000000	1.345453	-2.505463

[*a*,*f*]-DBP singlet C_{2v}

E = –615.8121777 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	-1.333422	1.964860
2	6	0	0.000000	-2.186428	0.839530
3	6	0	0.000000	-1.357460	-0.367816
4	6	0	0.000000	0.000000	0.063063
5	6	0	0.000000	0.000000	1.482898
6	6	0	0.000000	1.357460	-0.367816
7	6	0	0.000000	2.186428	0.839530
8	6	0	0.000000	1.333422	1.964860
9	1	0	0.000000	1.654882	2.998831
10	6	0	0.000000	3.592696	0.750150
11	1	0	0.000000	4.195068	1.652840
12	6	0	0.000000	4.188645	-0.496561
13	1	0	0.000000	5.267740	-0.589835
14	6	0	0.000000	3.387295	-1.663117
15	1	0	0.000000	3.878963	-2.630599
16	6	0	0.000000	1.999126	-1.615974
17	1	0	0.000000	1.425613	-2.535558
18	6	0	0.000000	-3.592696	0.750150
19	1	0	0.000000	-4.195068	1.652840
20	6	0	0.000000	-1.999126	-1.615974
21	6	0	0.000000	-4.188645	-0.496561
22	1	0	0.000000	-5.267740	-0.589835
23	6	0	0.000000	-3.387295	-1.663117
24	1	0	0.000000	-3.878963	-2.630599
25	1	0	0.000000	-1.654882	2.998831
26	1	0	0.000000	-1.425613	-2.535558

[*a*,*f*]-DBP singlet C_{2v} open-shell

E = –615.8137709 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	-1.335981	1.979735
2	6	0	0.000000	-2.188567	0.840749
3	6	0	0.000000	-1.360519	-0.357877
4	6	0	0.000000	0.000000	0.083176
5	6	0	0.000000	0.000000	1.504585
6	6	0	0.000000	1.360519	-0.357877
7	6	0	0.000000	2.188567	0.840749
8	6	0	0.000000	1.335981	1.979735
9	1	0	0.000000	1.664382	3.010969
10	6	0	0.000000	3.588509	0.739658
11	1	0	0.000000	4.201698	1.634839
12	6	0	0.000000	4.175885	-0.518139
13	1	0	0.000000	5.255029	-0.614853
14	6	0	0.000000	3.374694	-1.677014
15	1	0	0.000000	3.857175	-2.648598
16	6	0	0.000000	1.983043	-1.610903
17	1	0	0.000000	1.397322	-2.522893
18	6	0	0.000000	-3.588509	0.739658
19	1	0	0.000000	-4.201698	1.634839
20	6	0	0.000000	-1.983043	-1.610903
21	6	0	0.000000	-4.175885	-0.518139
22	1	0	0.000000	-5.255029	-0.614853
23	6	0	0.000000	-3.374694	-1.677014
24	1	0	0.000000	-3.857175	-2.648598
25	1	0	0.000000	-1.664382	3.010969
26	1	0	0.000000	-1.397322	-2.522893