

On Entangled Singlet Pure Diradicals

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Supporting information

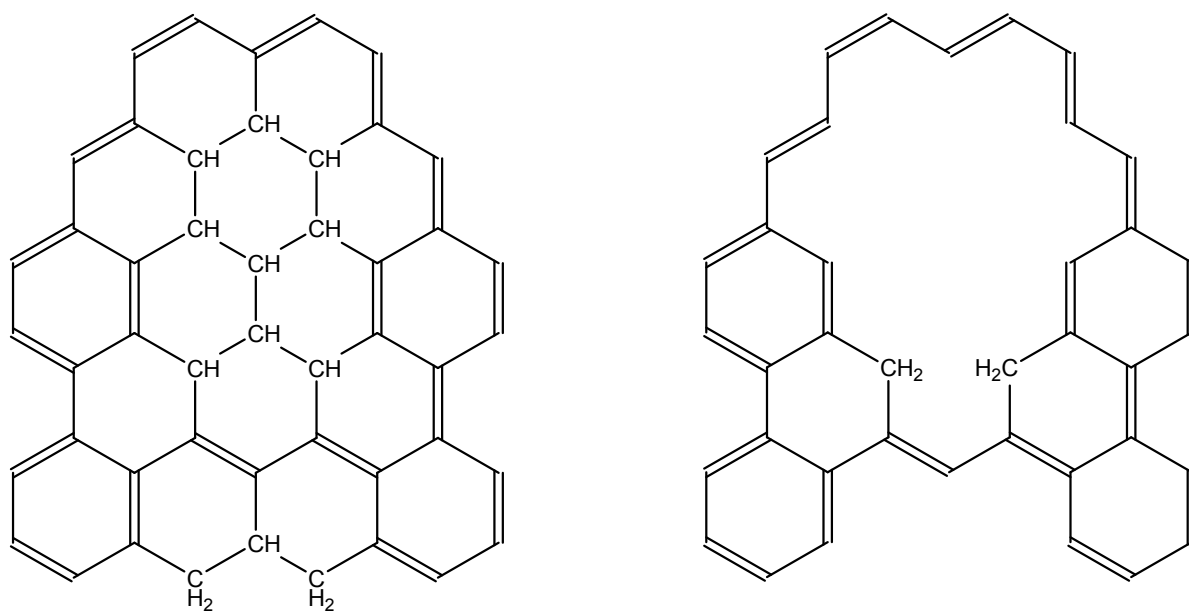


Figure S1. Flake **3-9** (left) and its less-graphanized variant (right) addressed for sake of comparisons.

Table S1. UDFT-calculated relative energies for flake **3-9** and its less-graphanized variant. Introduction of the sp^3 -carbon set in the graph induces only small changes in the energy differences.

	flake 3-9	“empty” variant
carbon atom count		
polyenic	12	12
polycyclic	24	24
total conjugated	36	36
graphanised	12	3
empirical formula	$C_{48}H_{30}$	$C_{39}H_{28}$
relative energies (kcal/mol)		
closed-shell singlet (vertical)	13.3	14.9
closed-shell singlet	9.0	9.9
triplet	0.9	0.7
BS $m_s=0$ (vert. closed-shell)	3.7	4.3
BS $m_s=0$	0.	0.

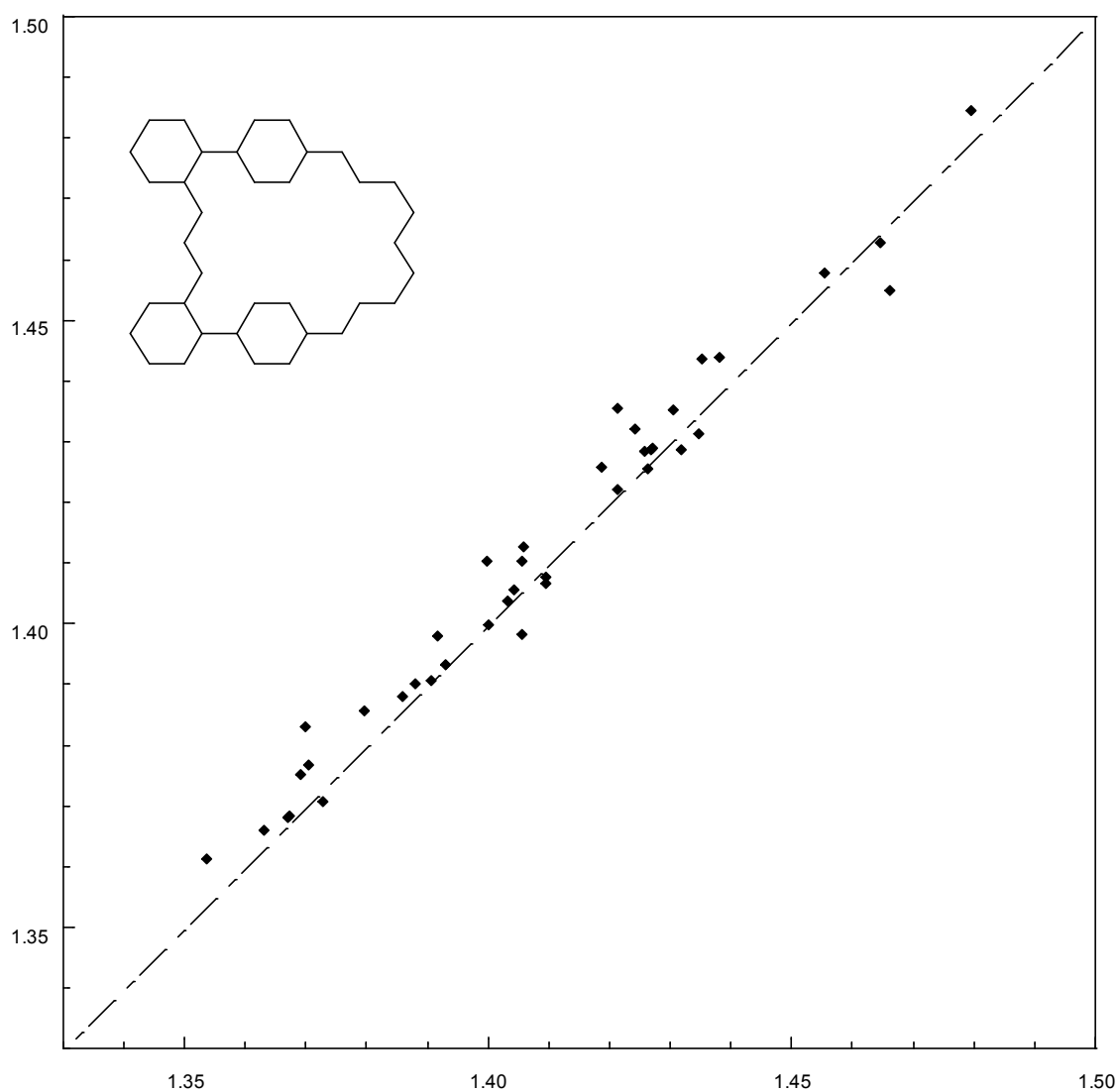


Figure S2. Effect of full graphanization on the conjugated frame geometry. Bond lengths in fully-graphanized flake **3-9** (ordinate) are compared with their equivalents in its less-graphanized variant (abscissa). Bond lengths in Å. Closed-shell solutions. Root-mean-square deviation: 0.006 Å; largest deviation: 0.014 Å.

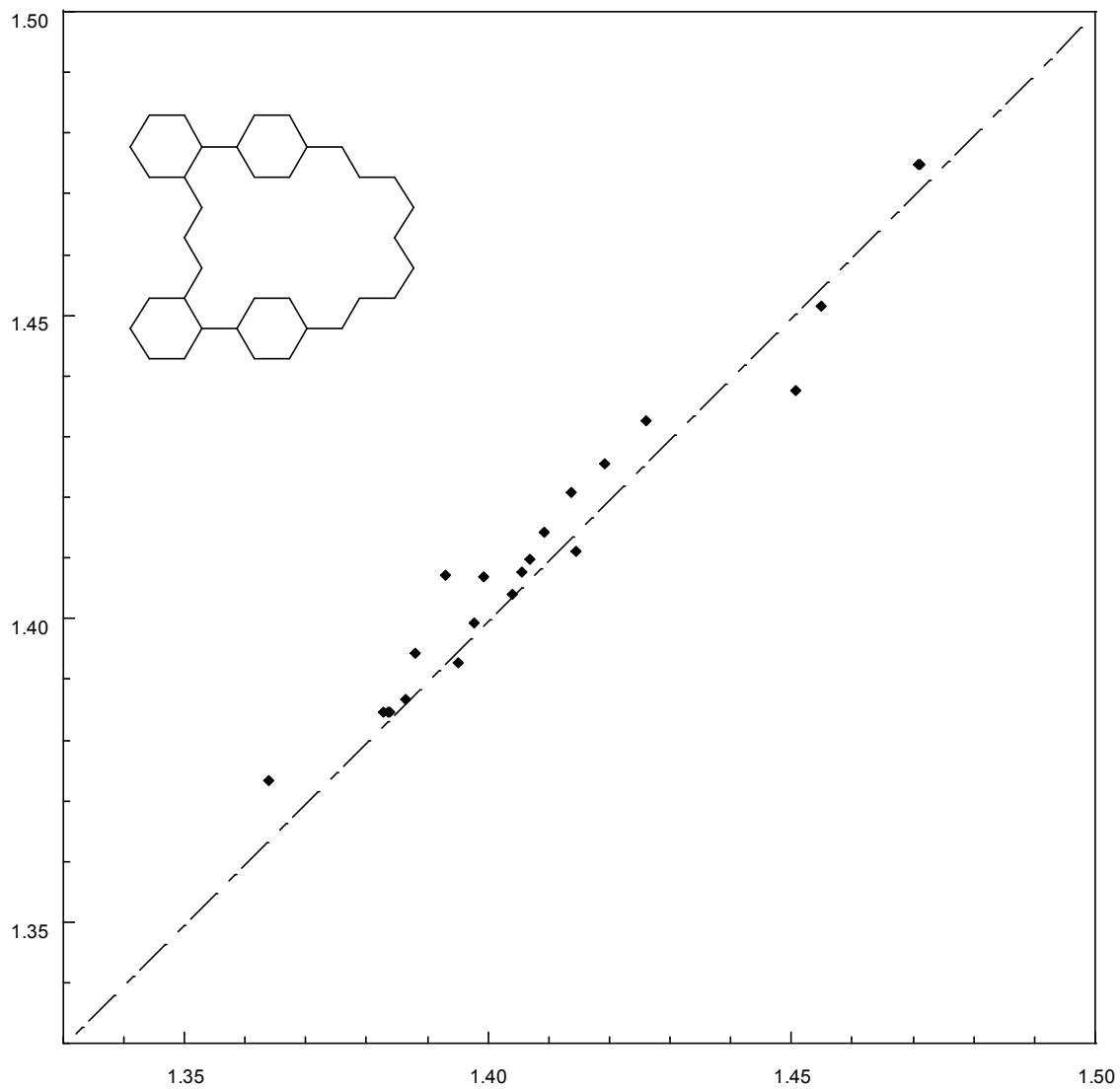


Figure S3. Effect of full graphanization on the conjugated frame geometry. Bond lengths in fully-graphanized flake **3-9** (ordinate) are compared with their equivalents in its less-graphanized variant (abscissa). Bond lengths in Å. BS $m_s=0$ solutions. Root-mean-square deviation: 0.006 Å; largest deviation: 0.014 Å.

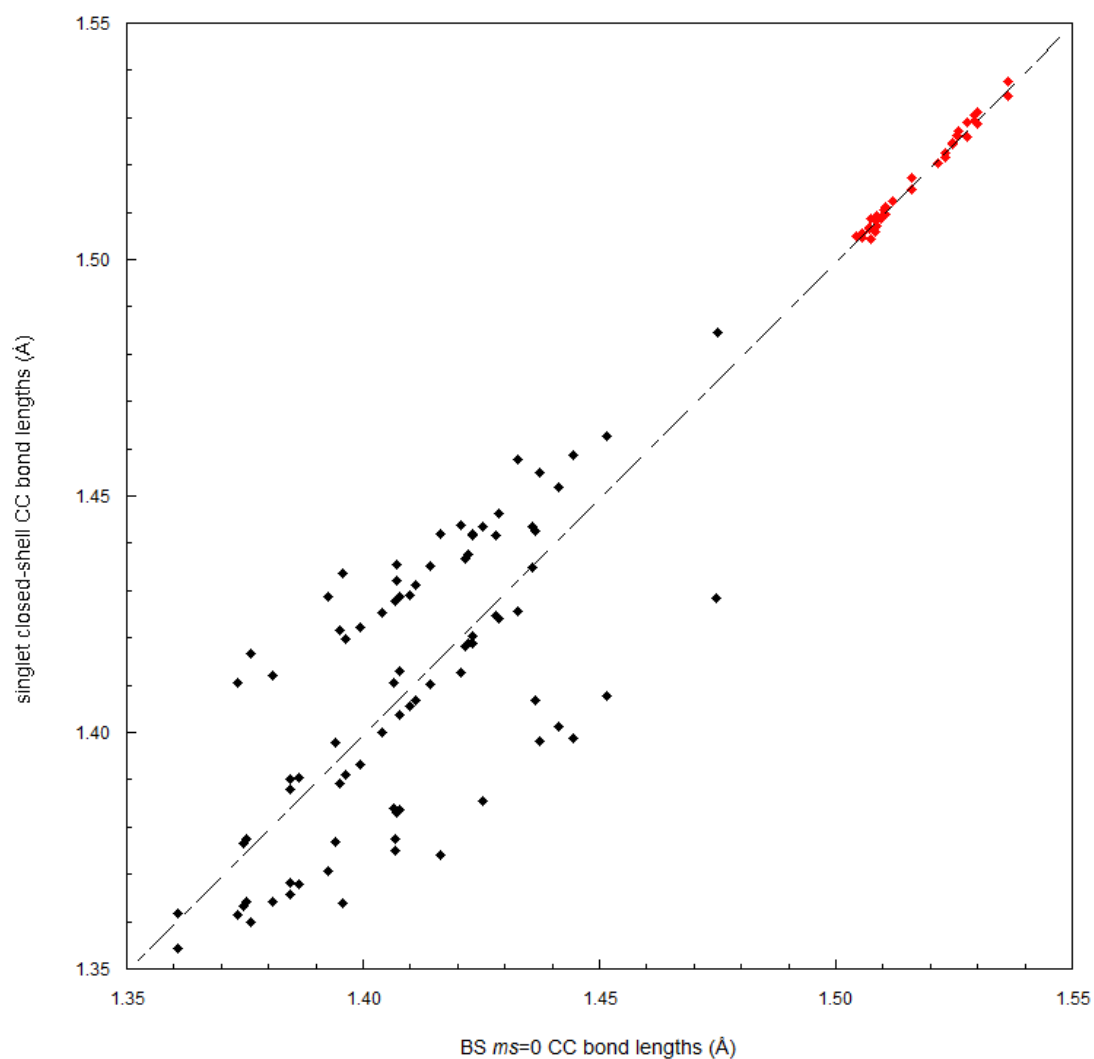


Figure S4. Illustrating how graphanized scaffolds (red points, corresponding to single bonds involving *saturated* carbon atoms) remains unaffected by configurational change, in contrast to the conjugated-bond set (black points). Both flakes **5-7** and **3-9** are included.

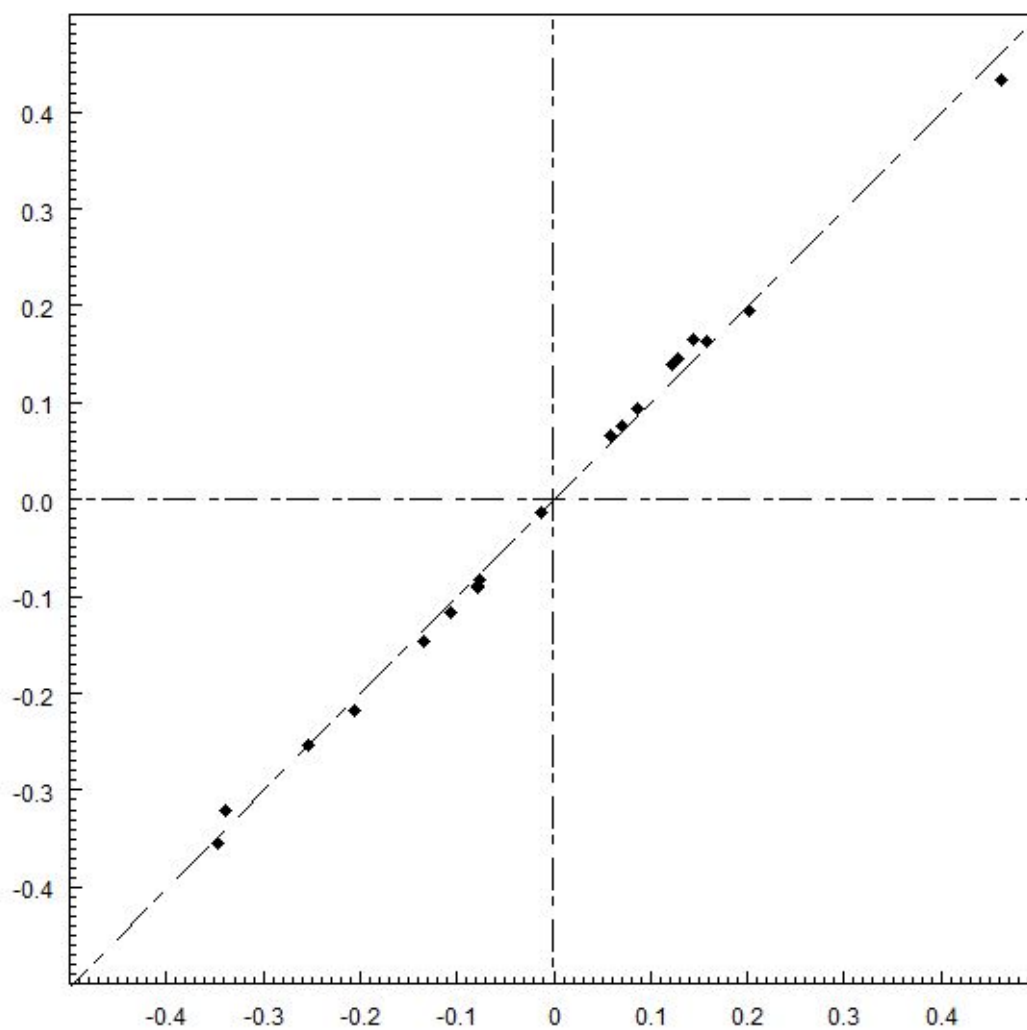
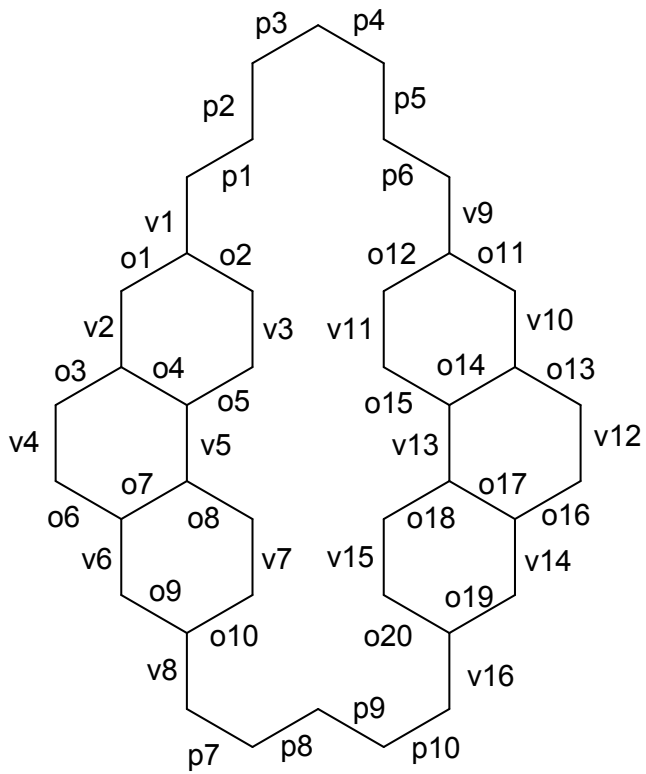


Figure S5. Effect of full graphanization on calculated spin densities. Total spin densities on conjugated carbon atoms for the BS $m_s=0$ solution in fully-graphanized flake **3-9** (ordinate) are compared with their equivalents in its less-graphanized variant (abscissa). Root-mean-square deviation: 0.013; largest deviation: 0.030.

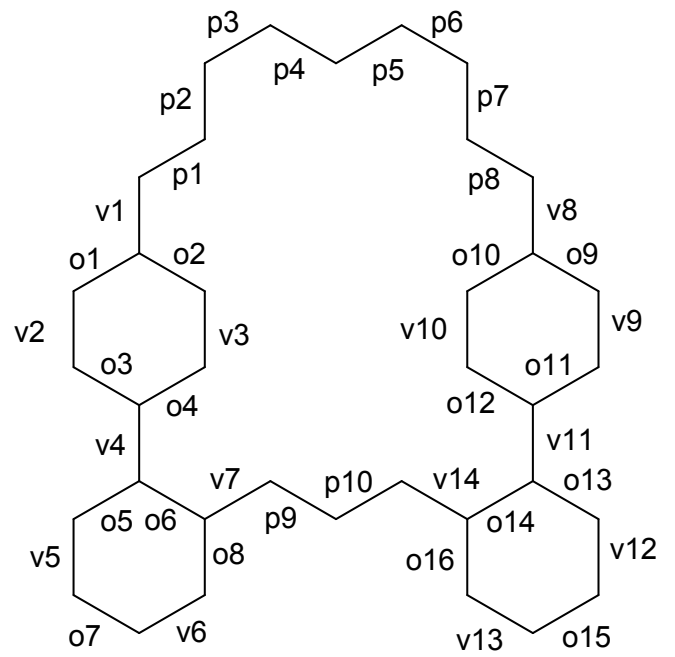
Table S2. Optimized lengths (in Å) of conjugated CC bonds in entangled diradicals. See diagrams below for bond labeling.

	flake 5-7		flake 3-9		
	BS $m_s=0$	cl.-sh.	BS $m_s=0$	cl.-sh.	
<i>p1</i>	1.376	1.360	<i>p1</i>	1.373	1.361
<i>p2</i>	1.416	1.442	<i>p2</i>	1.425	1.444
<i>p3</i>	1.396	1.364	<i>p3</i>	1.393	1.371
<i>p4</i>	1.396	1.434	<i>p4</i>	1.407	1.432
<i>p5</i>	1.416	1.374	<i>p5</i>	1.407	1.375
<i>p6</i>	1.376	1.417	<i>p6</i>	1.393	1.429
<i>p7</i>	1.396	1.364	<i>p7</i>	1.425	1.386
<i>p8</i>	1.441	1.428	<i>p8</i>	1.373	1.410
<i>p9</i>	1.381	1.377	<i>p9</i>	1.407	1.383
<i>p10</i>	1.407	1.412	<i>p10</i>	1.407	1.436
<i>v1</i>	1.445	1.459	<i>v1</i>	1.452	1.463
<i>v2</i>	1.408	1.413	<i>v2</i>	1.385	1.388
<i>v3</i>	1.375	1.377	<i>v3</i>	1.394	1.398
<i>v4</i>	1.361	1.362	<i>v4</i>	1.475	1.485
<i>v5</i>	1.437	1.443	<i>v5</i>	1.387	1.391
<i>v6</i>	1.406	1.411	<i>v6</i>	1.385	1.390
<i>v7</i>	1.375	1.377	<i>v7</i>	1.438	1.455
<i>v8</i>	1.441	1.452	<i>v8</i>	1.452	1.408
<i>v9</i>	1.445	1.399	<i>v9</i>	1.385	1.368
<i>v10</i>	1.408	1.384	<i>v10</i>	1.394	1.377
<i>v11</i>	1.375	1.363	<i>v11</i>	1.475	1.428
<i>v12</i>	1.361	1.354	<i>v12</i>	1.387	1.368
<i>v13</i>	1.437	1.407	<i>v13</i>	1.385	1.366
<i>v14</i>	1.406	1.384	<i>v14</i>	1.438	1.398
<i>v15</i>	1.375	1.364			
<i>v16</i>	1.441	1.401			
<i>o1</i>	1.395	1.389	<i>o1</i>	1.408	1.404
<i>o2</i>	1.429	1.424	<i>o2</i>	1.414	1.410
<i>o3</i>	1.436	1.435	<i>o3</i>	1.410	1.406
<i>o4</i>	1.423	1.419	<i>o4</i>	1.411	1.407
<i>o5</i>	1.422	1.419	<i>o5</i>	1.404	1.400
<i>o6</i>	1.436	1.435	<i>o6</i>	1.433	1.426
<i>o7</i>	1.423	1.420	<i>o7</i>	1.399	1.393
<i>o8</i>	1.422	1.418	<i>o8</i>	1.421	1.413
<i>o9</i>	1.396	1.391	<i>o9</i>	1.408	1.429
<i>o10</i>	1.428	1.425	<i>o10</i>	1.414	1.435
<i>o11</i>	1.395	1.422	<i>o11</i>	1.410	1.429
<i>o12</i>	1.429	1.446	<i>o12</i>	1.411	1.431
<i>o13</i>	1.436	1.444	<i>o13</i>	1.404	1.425
<i>o14</i>	1.423	1.442	<i>o14</i>	1.433	1.458
<i>o15</i>	1.422	1.438	<i>o15</i>	1.399	1.422
<i>o16</i>	1.436	1.443	<i>o16</i>	1.421	1.444

<i>o17</i>	1.423	1.442
<i>o18</i>	1.422	1.437
<i>o19</i>	1.396	1.420
<i>o20</i>	1.428	1.442



flake 5-7



flake 3-9

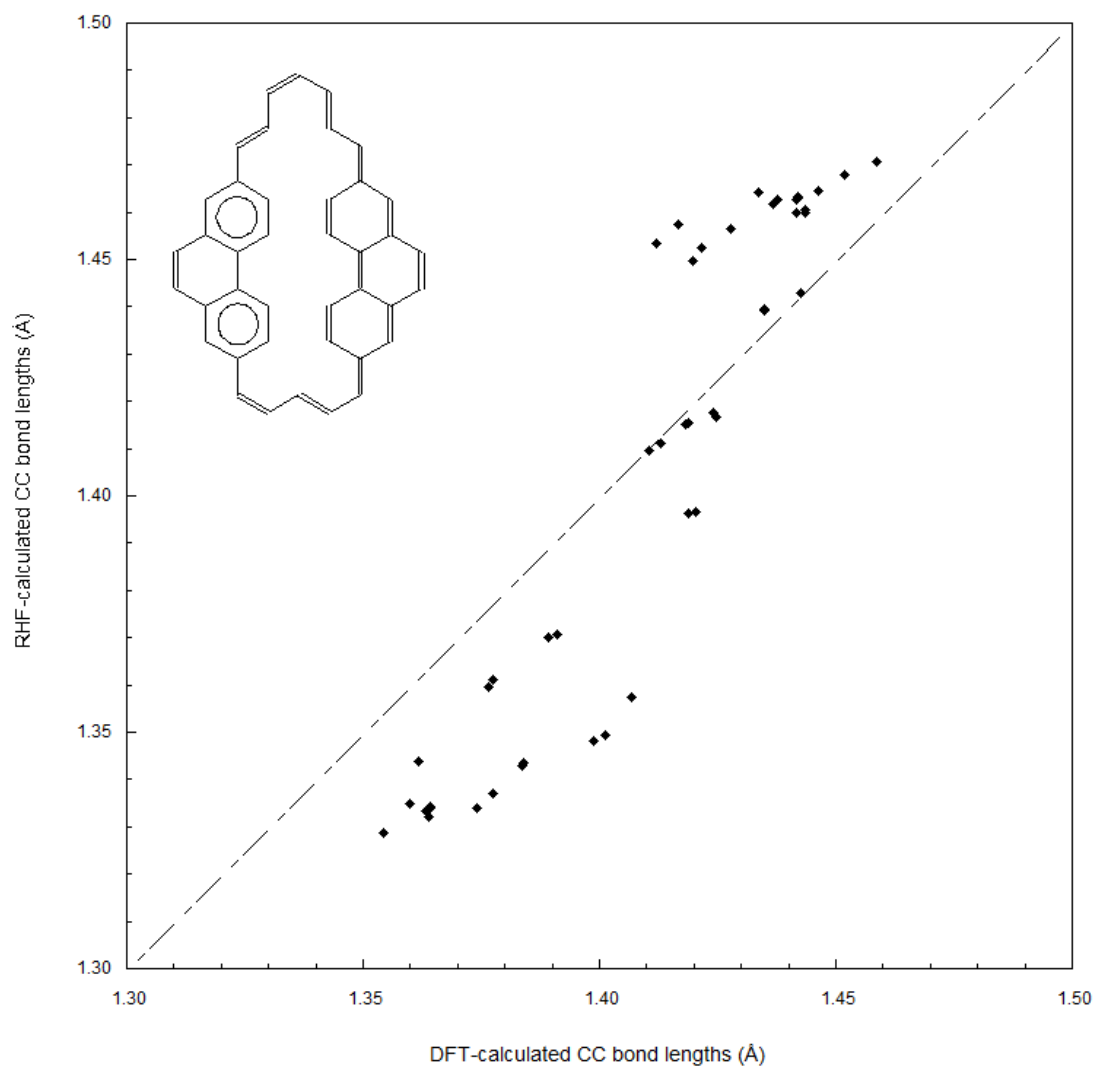


Figure S6. Comparing RHF and DFT geometries for the closed-shell solution of flake **5-7** (same basis set 6-311G** in both treatments). Contrast between short and long bonds is clearly stronger in HF

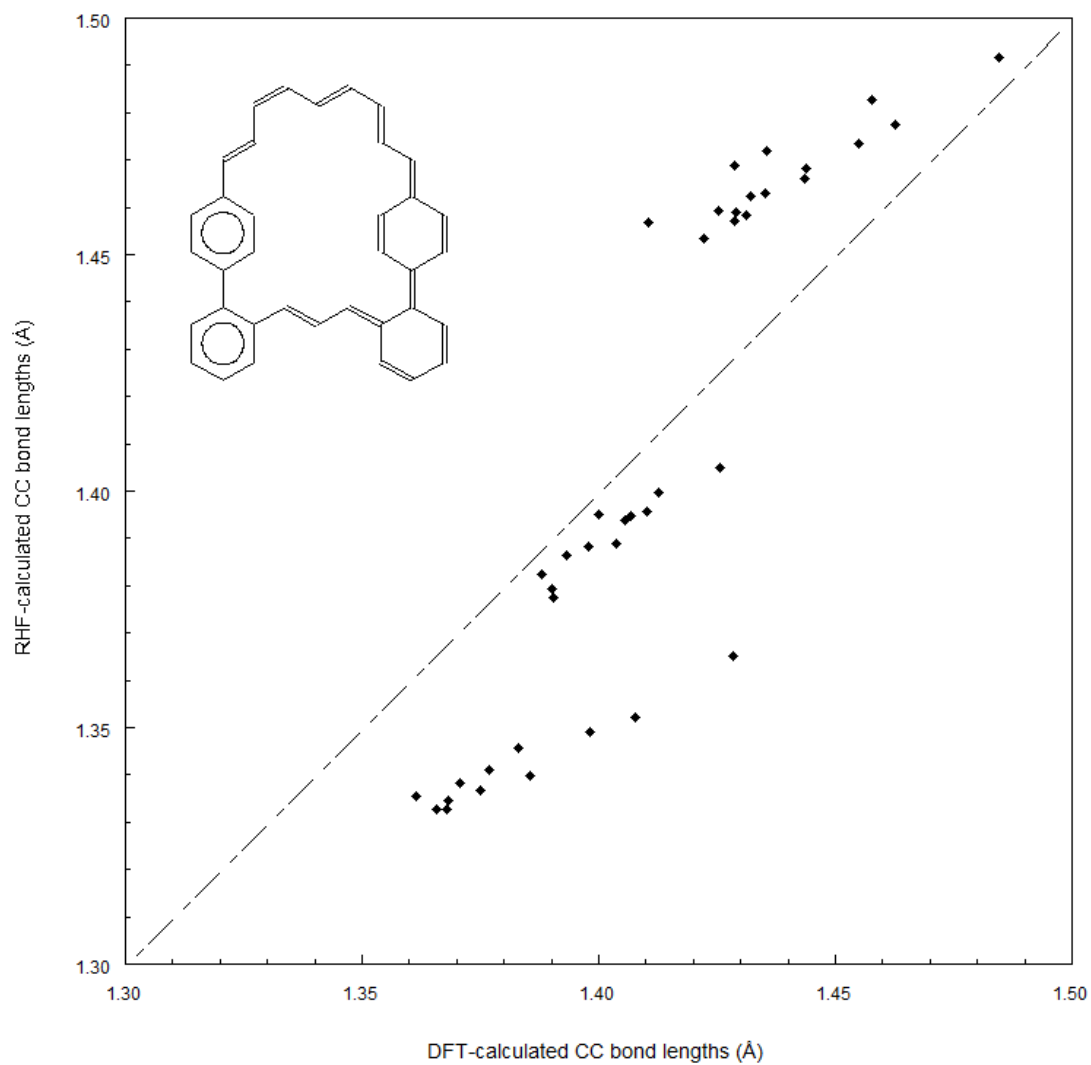
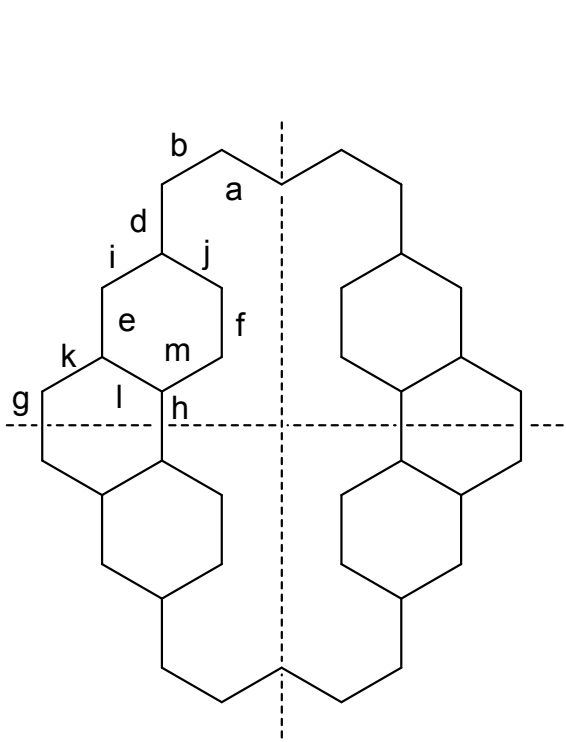


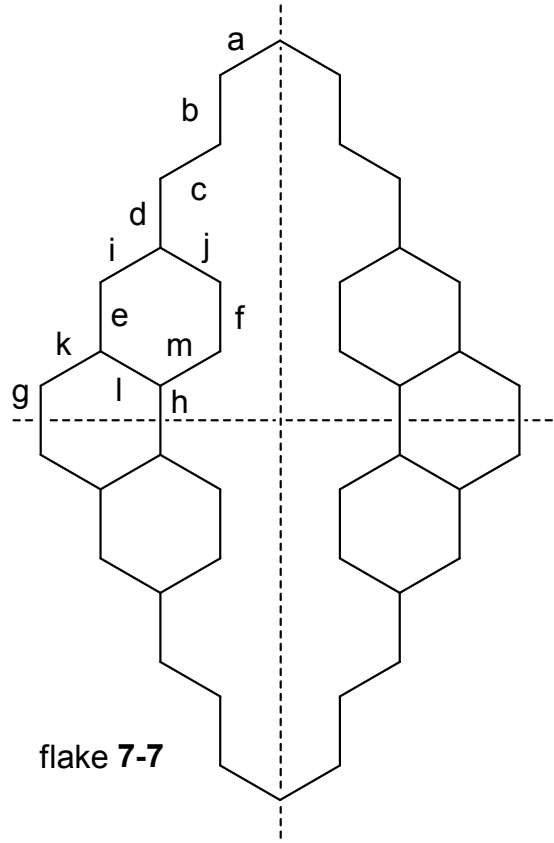
Figure S7. Comparing RHF and DFT geometries for the closed-shell solution of flake **3-9** (same basis set 6-311G** in both treatments). Again, contrast between short and long bonds is clearly stronger in HF.

Table S3. Optimized lengths (in Å) of conjugated CC bonds in diradicaloids. Flake **7-7**, the structure of which is detailed in Figure S8, is not discussed in the text and exhibits the same behaviour as flake **5-5**. See diagrams below for bond labeling.

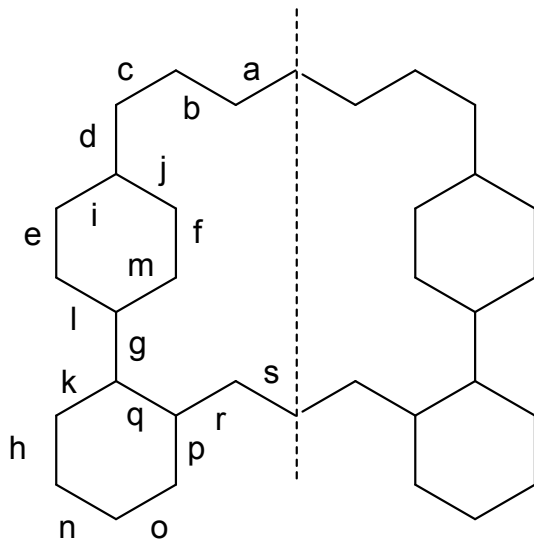
	flake 5-5		flake 7-7		flake 3-7		
	BS $m_s=0$	cl.-sh.	BS $m_s=0$	cl.-sh.	BS $m_s=0$	cl.-sh.	
<i>a</i>	1.404	1.400	1.396	1.396	<i>a</i>	1.400	1.400
<i>b</i>	1.383	1.388	1.415	1.405	<i>b</i>	1.413	1.405
<i>c</i>			1.377	1.385	<i>c</i>	1.377	1.385
<i>d</i>	1.435	1.424	1.442	1.428	<i>d</i>	1.441	1.427
<i>e</i>	1.403	1.395	1.407	1.399	<i>e</i>	1.382	1.378
<i>f</i>	1.374	1.370	1.374	1.369	<i>f</i>	1.393	1.386
<i>g</i>	1.359	1.357	1.361	1.359	<i>g</i>	1.471	1.454
<i>h</i>	1.432	1.423	1.434	1.423	<i>h</i>	1.384	1.376
<i>i</i>	1.399	1.406	1.396	1.404	<i>i</i>	1.408	1.413
<i>j</i>	1.429	1.433	1.430	1.435	<i>j</i>	1.413	1.419
<i>k</i>	1.437	1.440	1.436	1.438	<i>k</i>	1.407	1.415
<i>l</i>	1.426	1.432	1.424	1.430	<i>l</i>	1.411	1.416
<i>m</i>	1.424	1.428	1.423	1.428	<i>m</i>	1.413	1.420
					<i>n</i>	1.402	1.410
					<i>o</i>	1.382	1.375
					<i>p</i>	1.423	1.431
					<i>q</i>	1.434	1.441
					<i>r</i>	1.433	1.422
					<i>s</i>	1.406	1.406



flake 5-5



flake 7-7



flake 3-7

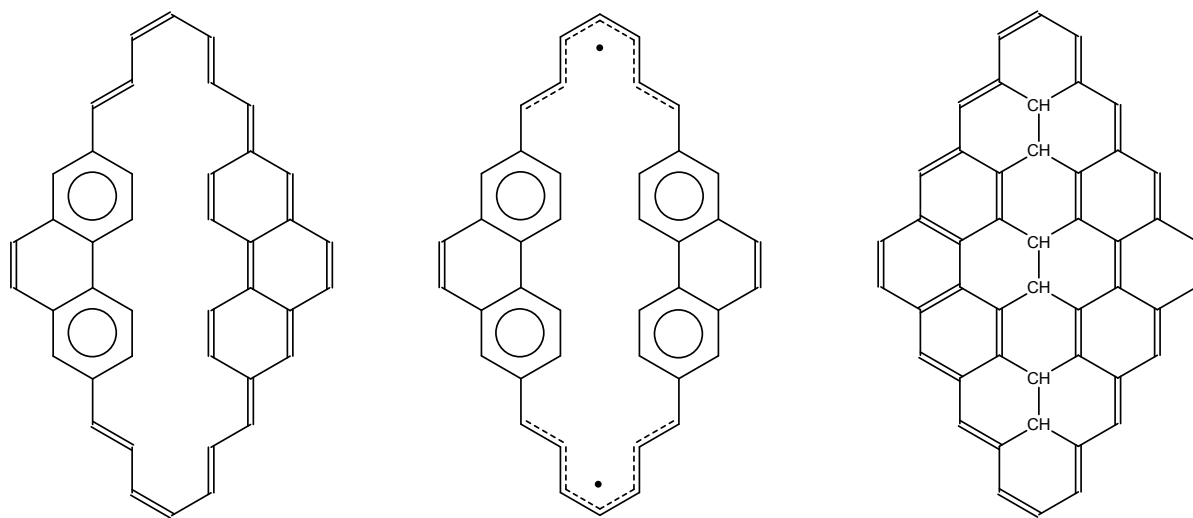


Figure S8. Flake 7-7 drawn with the same conventions as in Figure S1.