Supporting Information

A Computational Study of Tetrafluoro-[2.2]Cyclophanes

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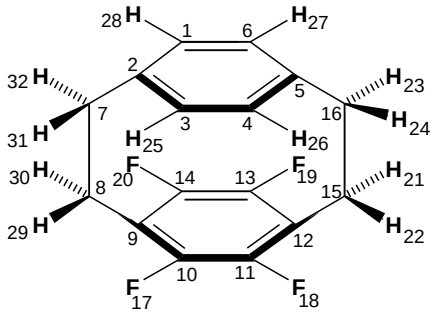
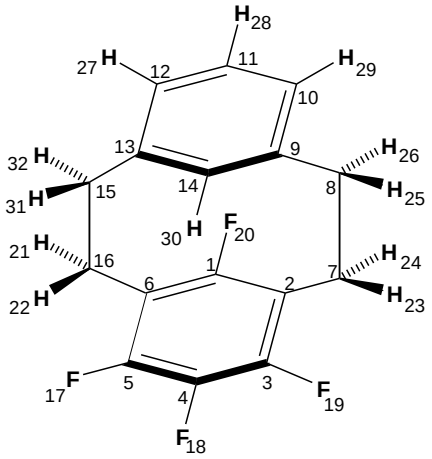
Table S1 Geometric parameters of **4**



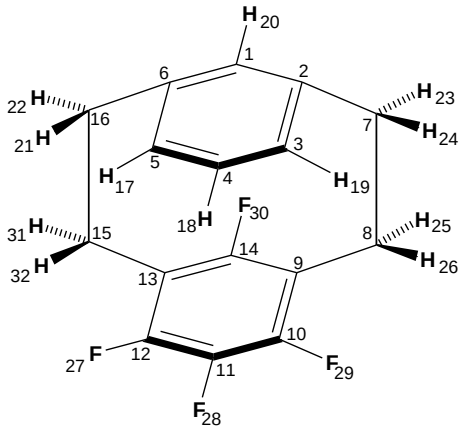
distances (Å)		bond angles (°)		dihedrals (°)	
C(1)C(2)	1.401	C(1)C(2)C(3)	117.0	C(1)C(2)C(3)C(4)	-14.0
C(1)C(14)	3.068	C(1)C(2)C(7)	121.6	C(2)C(3)C(4)C(5)	0.4
C(2)C(3)	1.403	C(2)C(3)C(4)	121.0	C(2)C(3)C(4)H(26)	-172.0
C(2)C(7)	1.512	C(2)C(7)C(8)	112.4	C(2)C(7)C(8)C(9)	6.4
C(2)C(9)	2.779	C(2)C(7)H(31)	109.0	C(2)C(7)C(8)H(29)	128.6
C(3)C(4)	1.395	C(2)C(7)H(32)	112.2	C(5)C(4)C(3)H(25)	171.3
C(3)C(10)	3.039	C(3)C(2)C(7)	120.1	C(9)C(10)C(11)F(18)	170.6
C(7)C(8)	1.588	C(3)C(4)C(5)	120.5	C(9)C(10)C(11)C(12)	0.2
C(8)C(9)	1.513	C(7)C(8)C(9)	111.9	C(12)C(11)C(10)F(17)	-169.9
C(9)C(10)	1.391	C(8)C(9)C(10)	121.5	C(14)C(9)C(10)C(11)	11.0
C(10)C(11)	1.392	C(8)C(9)C(14)	120.7	C(5)C(16)C(15)C(12)	6.4
C(11)C(12)	1.394	C(9)C(8)H(29)	111.6	H(25)C(3)C(4)H(26)	-0.3
C(10)F(17)	1.348	C(9)C(8)H(30)	108.3	H(26)C(4)C(5)C(6)	174.2
C(1)H(28)	1.088	C(9)C(10)C(11)	121.8	H(32)C(7)C(8)H(29)	-100.7
C(7)H(31)	1.094	C(11)C(12)C(13)	115.5	F(17)C(10)C(11)F(18)	0.6
C(7)H(32)	1.096	H(25)C(3)C(4)	119.0	F(18)C(11)C(12)C(13)	178.5
C(8)H(29)	1.094	F(17)C(10)C(9)	119.2	-	-
C(8)H(30)	1.092	F(17)C(10)C(11)	118.3	-	-
-	-	F(20)C(14)C(9)	119.8	-	-

Table S2. Geometric parameters of **5a**



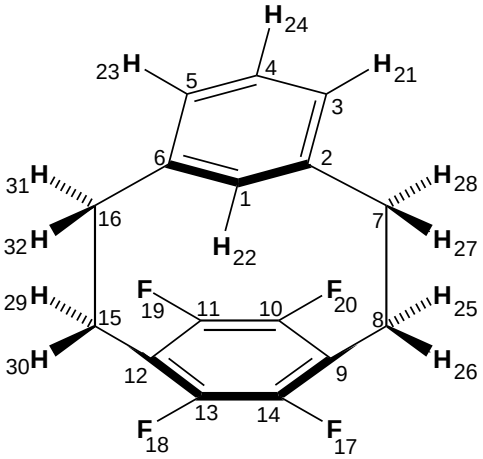
distances (Å)		bond angles (°)		dihedrals (°)	
C(1)C(2)	1.405	C(1)C(2)C(3)	118.3	C(1)C(2)C(3)C(4)	-1.6
C(1)C(14)	2.611	C(1)C(6)C(16)	119.1	C(2)C(1)C(6)C(5)	-8.8
C(1)F(20)	1.087	C(2)C(3)C(4)	120.4	C(2)C(3)C(4)C(5)	-5.3
C(2)C(3)	1.403	C(2)C(1)F(20)	118.9	C(2)C(7)C(8)C(9)	59.5
C(2)C(7)	1.505	C(2)C(3)F(19)	119.6	C(2)C(7)C(8)H(25)	61.8
C(4)F(18)	1.084	C(3)C(4)C(5)	120.0	C(6)C(16)C(15)C(13)	59.5
C(5)F(17)	1.086	C(5)C(6)C(16)	121.0	C(7)C(2)C(1)F(20)	15.2
C(7)C(8)	1.567	C(6)C(1)C(2)	121.6	C(7)C(2)C(3)F(19)	-15.3
C(7)H(24)	1.094	C(9)C(10)H(29)	119.6	C(8)C(9)C(10)H(29)	-15.2
C(11)C(12)	1.400	C(9)C(14)H(30)	118.9	C(10)C(9)C(14)C(13)	9.0
C(11)H(28)	1.084	C(10)C(9)C(14)	118.3	C(10)C(11)C(12)C(13)	5.3
C(12)C(13)	1.403	C(11)C(12)C(13)	120.4	C(11)C(10)C(9)C(14)	-1.8
C(13)C(14)	1.405	C(12)C(13)C(15)	121.0	F(17)C(5)C(4)F(18)	2.5

Table S3. Geometric parameters of **5b**



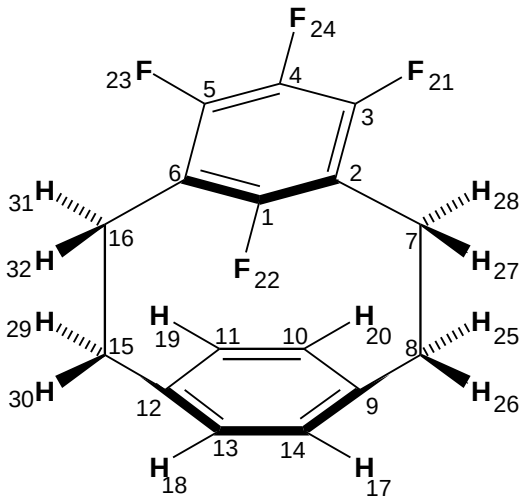
distances (Å)		bond angles (°)		dihedrals (°)	
C(1)C(2)	1.399	C(1)C(2)C(3)	117.9	C(1)C(2)C(3)C(4)	3.7
C(1)C(14)	2.711	C(1)C(2)C(7)	118.0	C(2)C(3)C(4)C(5)	5.8
C(1)H(20)	1.086	C(2)C(1)C(6)	122.1	C(2)C(7)C(8)C(9)	19.5
C(2)C(3)	1.400	C(2)C(1)H(20)	118.5	C(2)C(7)C(8)H(25)	142.8
C(2)C(9)	2.836	C(2)C(3)H(19)	120.1	C(2)C(7)C(8)H(26)	-101.2
C(2)C(7)	1.510	C(2)C(3)C(4)	120.0	C(3)C(2)C(7)C(8)	81.26
C(3)C(4)	1.396	C(2)C(7)C(8)	113.5	C(3)C(4)C(5)C(6)	-6.3
C(4)C(11)	4.189	C(2)C(7)H(24)	111.3	C(7)C(8)C(9)C(10)	-105.6
C(4)H(18)	1.087	C(3)C(4)C(5)	120.4	C(7)C(8)C(9)C(14)	59.2
C(5)H(17)	1.088	C(7)C(8)C(9)	113.6	C(8)C(9)C(10)F(29)	-15.2
C(7)C(8)	1.590	C(8)C(9)C(10)	122.2	C(9)C(10)C(11)C(12)	-5.7
C(7)H(23)	1.094	C(9)C(10)C(11)	122.2	C(9)C(10)C(11)F(28)	179.2
C(8)C(9)	1.510	C(9)C(10)F(29)	120.1	C(10)C(11)C(12)C(13)	5.5
C(8)H(25)	1.094	C(9)C(14)C(13)	125.3	C(12)C(13)C(14)C(9)	-13.8
C(9)C(10)	1.394	C(9)C(1)4F(30)	116.4	H(17)C(5)C(4)H(18)	-3.5
C(9)C(14)	1.395	C(9)C(8)H(25)	110.7	H(17)C(5)C(6)C(1)	179.5
C(10)C(11)	1.392	C(9)C(8)H(26)	108.0	H(23)C(7)C(8)H(25)	21.5
C(10)F(29)	1.344	C(10)C(11)C(12)	118.9	H(23)C(7)C(8)H(26)	137.6
C(11)F(28)	1.339	C(10)C(11)F(28)	120.4	F(27)C(12)C(11)F(28)	3.8
C(14)F(30)	1.358				

Table S4. Geometric parameters of **6a**



distances (Å)		bond angles (°)		dihedrals (°)	
C(1)C(2)	1.402	C(1)C(2)C(3)	117.8	C(1)C(2)C(3)C(4)	-2.8
C(1)H(22)	1.087	C(1)C(2)C(7)	119.6	C(1)C(2)C(7)C(8)	36.21
C(2)C(3)	1.399	C(2)C(3)C(4)	120.4	C(2)C(3)C(4)C(5)	-4.4
C(2)C(7)	1.517	C(2)C(7)C(8)	113.2	C(2)C(3)C(4)H(24)	179.2
C(3)C(4)	1.396	C(2)C(7)H(27)	109.3	C(2)C(7)C(8)C(9)	-38.6
C(3)H(21)	1.088	C(3)C(4)C(5)	120.5	C(2)C(7)C(8)H(25)	80.9
C(4)H(24)	1.087	C(3)C(4)H(24)	119.7	C(2)C(7)C(8)H(26)	-161.1
C(7)C(8)	1.577	C(7)C(8)C(9)	108.9	C(7)C(8)C(9)C(10)	90.8
C(7)H(27)	1.095	C(7)C(8)H(26)	109.0	C(7)C(8)C(9)C(14)	-67.2
C(8)C(9)	1.509	C(8)C(9)C(10)	120.1	C(8)C(9)C(10)F(20)	24.8
C(8)H(26)	1.093	C(8)C(9)C(14)	121.0	C(8)C(9)C(14)F(17)	-22.2
C(9)C(10)	1.395	C(9)C(10)C(11)	121.6	C(9)C(10)C(11)C(12)	0.0
C(10)C(11)	1.390	C(9)C(10)F(20)	119.7	C(10)C(11)C(12)C(13)	-13.1
C(10)F(20)	1.345	C(10)C(9)C(14)	115.5	H(21)C(3)C(4)H(24)	-2.6
C(11)F(19)	1.345	C(10)C(11)C(12)	121.6	F(19)C(11)C(10)F(20)	0.0
C(14)F(17)	1.348	C(10)C(11)F(19)	118.2	F(17)C(14)C(13)F(18)	0.0

Table S5. Geometric parameters of **6b**



distances (Å)		bond angles (°)		dihedrals (°)	
C(1)C(2)	1.402	C(1)C(2)C(3)	115.1	C(1)C(2)C(3)C(4)	2.80
C(1)F(22(	1.348	C(1)C(2)C(7)	121.8	C(1)C(2)C(7)C(8)	87.2
C(2)C(3)	1.400	C(2)C(3)C(4)	122.3	C(2)C(3)C(4)C(5)	4.41
C(2)C(7)	1.517	C(2)C(7)C(8)	112.2	C(2)C(3)C(4)F(24)	178.8
C(3)C(4)	1.396	C(2)C(7)H(27)	108.4	C(2)C(7)C(8)C(9)	37.4
C(3)F(21)	1.348	C(3)C(4)C(5)	118.9	C(2)C(7)C(8)H(25)	83.2
C(4)F(24)	1.348	C(3)C(4)F(24)	120.5	C(2)C(7)C(8)H(26)	160.3
C(7)C(8)	1.577	C(7)C(8)C(9)	109.4	C(7)C(8)C(9)C(10)	90.5
C(7)H(27)	1.095	C(7)C(8)H(26)	107.9	C(7)C(8)C(9)C(14)	71.7
C(8)C(9)	1.509	C(8)C(9)C(10)	119.5	C(8)C(9)C(10)H(20)	22.6
C(8)H(26)	1.094	C(8)C(9)C(14)	120.8	C(8)C(9)C(14)H(17)	23.2
C(9)C(10)	1.396	C(9)C(10)C(11)	120.4	C(9)C(10)C(11)C(12)	1.0
C(10)C(11)	1.390	C(9)C(10)H(20)	119.7	C(10)C(11)C(12)C(13)	15.6
C(10)H(20)	1.080	C(10)C(9)C(14)	117.4	F(21)C(3)C(4)F(24)	2.7
C(11)H(19)	1.080	C(10)C(11)C(12)	120.4	H(19)C(11)C(10)H(20)	1.0
C(14)H(17)	1.080	C(10)C(11)H(19)	119.3	H(17)C(14)C(13)H(18)	1.0

Table S6: Electronic energies (E), zero point energy (ZPE), total energy (E+ZPE), and relative energy (ΔE), (Hartree), of the [2.2]cyclophanes **1-3** and **4-6b**, by B3PW91/6-31+G(d,p).

Isomers	E(hartree)	ZPE(hartree)	E + ZPE(hartree)	ΔE(hartree)
4	-1015.9110588	0.242467	-1015.668592	0.0244032
5a	-1015.9361110	0.243116	-1015.692995	0.0000000
5b	-1015.9231776	0.244255	-1015.678923	0.0140724
6a	-1015.9228701	0.243033	-1015.679837	0.0131579
6b	-1015.9208906	0.242839	-1015.678052	0.0149434
1	-619.1073766	0.274267	-618.833109	0.0328030
2a	-619.1417279	0.275815	-618.865912	0.0000000
2b	-619.123083	0.275012	-618.848071	0.0178410
3	-619.1255004	0.275023	-618.850477	0.0154350

Table S7: Electronic energies (E), and total energy (E+ZPE), (Hartree), of the [2.2]cyclophanes **1**-**3** and **4**-**6b**, by MP2. SCS-MP2 and SOS-MP2 with 6-31+G(d,p) basis.

Isomers	MP2		SCS-MP2		SOS-MP2	
	E	E+ZPE	E	E+ZPE	E	E+ZPE
4	-1013.468144	-1013.2256773	-1013.364727	-1013.1222596	-1013.313018	-1013.0705507
5a	-1013.487070	-1013.2439541	-1013.384741	-1013.1416253	-1013.333577	-1013.0904609
5b	-1013.475140	-1013.2308846	-1013.372893	-1013.1286376	-1013.321769	-1013.0775141
6a	-1013.479894	-1013.2368606	-1013.376703	-1013.1336698	-1013.325107	-1013.0820744
6b	-1013.478026	-1013.2351872	-1013.374702	-1013.1318635	-1013.323041	-1013.0802016
1	-617.395702	-617.1214353	-617.336236	-617.0619688	-617.306232	-617.0319647
2a	-617.423284	-617.1474695	-617.362709	-617.0868944	-617.333476	-617.0576613
2b	-617.405593	-617.1305811	-617.343976	-617.0689635	-617.314919	-617.0399066
3	-617.413106	-617.1380826	-617.350508	-617.0754848	-617.320788	-617.0457655

Table S8. Calculated and experimental chemical shifts, ^{1}H (ppm), of the F_4-[2.2]paracyclophanes.

	(B3PW91/6-31+G(d.p))				Experimental[43,44]			
Comp.	Ring (I)		Bridges		Ring (I)		Bridges	
4	H(25)	7.23	H(21)	3.01	H(25)	6.84	H(21)	2.98
	H(26)	7.23	H(22)	3.00	H(26)	6.84	H(22)	2.98
	H(27)	7.23	H(23)	2.99	H(27)	6.84	H(23)	3.07
	H(28)	7.22	H(24)	3.11	H(28)	6.84	H(24)	3.07
5a	H(27)	7.46	H(23)	3.18				
	H(28)	7.60	H(24)	2.39				
	H(29)	7.44	H(25)	2.39				
	H(30)	4.62	H(26)	2.91				
5b	H(17)	6.90	H(23)	2.97				
	H(18)	7.17	H(24)	3.01				
	H(19)	6.98	H(25)	2.91				
	H(20)	7.43	H(26)	3.02				
6a	H(21)	7.26	H(25)	3.04	H(21)	6.82	H(25)	-
	H(22)	6.26	H(26)	3.08	H(22)	5.78	H(26)	-
	H(23)	7.27	H(27)	2.61	H(23)	6.82	H(27)	-
	H(24)	7.40	H(28)	2.85	H(24)	7.01	H(28)	-
6b	H(17)	6.46	H(25)	2.71				
	H(18)	6.48	H(26)	3.08				
	H(19)	7.62	H(27)	2.69				
	H(20)	7.64	H(28)	2.74				

Table S9. Calculated and experimental chemical shifts, ^{13}C (ppm), of the F_4-[2.2]paracyclophanes.

Comp.	(B3PW91/6-31+G(d.p))						Experimental[43,44]					
	Ring (I)		Ring (II)		Bridges		Ring (I)		Ring (II)		Bridges	
4	C(1)	127.06	C(9)	118.34	C(7)	37.14	C(1)	129.62	C(9)	118.80	C(7)	32.92
	C(2)	137.01	C(10)	145.43	C(8)	25.62	C(2)	139.05	C(10)	146.40	C(8)	21.99
	C(3)	127.63	C(11)	147.77	C(15)	25.62	C(3)	129.62	C(11)	146.40	C(15)	21.99
	C(4)	127.07	C(12)	118.34	C(16)	37.14	C(4)	129.62	C(12)	118.80	C(16)	32.92
	C(5)	137.03	C(13)	145.34			C(5)	139.05	C(13)	146.40		
	C(6)	127.63	C(14)	145.68			C(6)	129.62	C(14)	146.40		
5a	C(9)	136.12	C(1)	154.48	C(7)	31.21	-					
	C(10)	123.61	C(2)	112.22	C(8)	41.84						
	C(11)	126.12	C(3)	147.37	C(15)	41.61						
	C(12)	123.61	C(4)	136.87	C(16)	31.20						
	C(13)	136.22	C(5)	147.33								
	C(14)	127.01	C(6)	112.63								
5b	C(1)	129.37	C(9)	111.47	C(7)	35.14						
	C(2)	136.98	C(10)	148.14	C(8)	27.20						
	C(3)	123.02	C(11)	135.76	C(15)	26.09						
	C(4)	125.51	C(12)	148.21	C(16)	38.20						
	C(5)	124.94	C(13)	111.64								
	C(6)	138.08	C(14)	154.98								
6a	C(1)	127.55	C(9)	117.46	C(7)	36.58	C(1)	131.30	C(9)	118.10	C(7)	33.30
	C(2)	136.19	C(10)	147.39	C(8)	29.40	C(2)	138.50	C(10)	146.00	C(8)	34.90
	C(3)	123.36	C(11)	147.61	C(15)	28.99	C(3)	126.30	C(11)	146.00	C(15)	24.90
	C(4)	125.07	C(12)	116.55	C(16)	36.23	C(4)	127.00	C(12)	118.10	C(16)	33.30
	C(5)	123.75	C(13)	149.46			C(5)	126.30	C(13)	146.00		
	C(6)	135.39	C(14)	148.43			C(6)	138.50	C(14)	146.00		
6b	C(9)	135.35	C(1)	156.16	C(7)	26.71						
	C(10)	124.20	C(2)	112.73	C(8)	37.99						
	C(11)	124.21	C(3)	148.29	C(15)	38.14						
	C(12)	135.46	C(4)	136.77	C(16)	26.67						
	C(13)	127.70	C(5)	148.48								
	C(14)	127.73	C(6)	112.00								