Supplementary data for article:

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Supplementary information

Supplementary information for in/out isomerism of cyclophanes: a theoretical account on 2,6,15-trithia-[3^{4,10}][7]metacyclophane and [3^{4,10}][7]metacyclophane, as well as their halogen substituted analogues

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S1 Additional computational details

Additional calculations were performed using molecular mechanics as implemented in the Avogadro[1, 2] program using MMFF94[3] force field and steepest descent algorithm. Also, Density Functional based Tight Binding[4] (DFTB) method as implemented within the DFTB+[5] program was employed for structural optimization, including and excluding the Lennard-Jones dispersion correction scheme.[6] In DFTB calculations maximum angular momentum for second and third row elements was set to p or d in order to compare the difference in DFTB2 and DFTB3 application for crowded and strained molecules. There results are shown in Tables S1, S2, S3 and S4.

S2 Additional results

In tables S1 through S4 additional results are given in regards to MM and DFTB calculations, as well as LDA/6-31G(d). In Tables S3 and S4 list C3-C and C3-S bond lengths for all employed methods. Tables S5 through S8 list EDA-NOCV results on various geometries of *in/out*- 2,6,15-trithia-[3^{4,10}][7]metacyclophane and *in/out*- [3^{4,10}][7]metacyclophane and their halogen substituted analogues, as explained in the main text. SAPT results on model systems are shown in Tables S9 and S10, and EDA-NOCV results on model systems are presented in Tables S11 and S12. Most important contours of deformation density channels obtained via NOCV analysis on *in/out*- 2,6,15-trithia-[3^{4,10}][7]metacyclophane and its halogen substituted analogues, as well as the crystal structure of 2,6,15-trithia-[3^{4,10}][7]metacyclophane are shown in Figures S1 and S2. Most important contours of deformation density channels obtained via NOCV analysis on model systems are shown in Figures S3 and S2.

Table S1. Comparison of calculated nonbonded contacts[a,b] and relative energies[c] of *in/out*- 2,6,15-trithia-[3^{4,10}][7]metacyclophane and their fluorine, chlorine and bromine containing analogues

Method		*in*-H	*out*-H	*in*-F	*out*-F	*in*-Cl	*out*-Cl	*in*-Br	*out*-Br
	C1-C5	3.256	3.581	3.495	3.617	4.142	3.666	4.382	3.582
MMFF94	C2-C5	3.338	3.650	3.597	3.685	4.266	3.736	4.506	3.650
	ΔE_{in-out}		-0.78		37.72		188.38		263.95
	C1-C5	3.158	3.648	3.622	3.641	4.281	3.675	_d	3.719
DFTB	C2-C5	3.193	3.677	3.686	3.669	4.334	3.705	_d	3.750
	ΔE_{in-out}		-2.22		41.04		149.36		_d
DFTB –Lennard	C1-C5	3.254	3.732	3.646	3.732	_d	3.756	_d	3.807
Jones Dispersion	C2-C5	3.295	3.767	3.71	3.766	_d	3.791	_d	3.843
	ΔE_{in-out}		-3.47		37.34		_d		_d
DFTB	C1-C5	3.159	3.649	3.637	3.645	_d	3.659	_d	3.718
max. angular	C2-C5	3.194	3.677	3.701	3.672	_d	3.688	_d	3.748
momentum value d [d]	ΔE_{in-out}		-2.33		38.94		_d		_d
LDA/	C1-C5	3.077	3.610	3.575	3.593	4.034	3.623	4.263	3.618
6-31G(d)	C2-C5	3.110	3.637	3.635	3.620	4.086	3.650	4.266	3.644
	ΔE_{in-out}		-7.76		32.30		113.79		144.71

a- Nonbonded contacts are given in Å b- labelling of atoms is given in Figure 3 c- Relative energies between the two isomers ΔE_{in-out} in kcal/mol d- Employed method failed to optimize these isomers d- maximum angular momentum value for S, Cl and Br set to d

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Table S2. Comparison of calculated nonbonded contacts[a,b] and relative energies[c] of *in/out*-[3⁴,¹⁰][7]metacyclophane and their fluorine, chlorine and bromine containing analogues

Method		*in*-H	*out*-H	*in*-F	*out*-F	*in*-Cl	*out*-Cl	*in*-Br	*out*-Br
MMFF94	C1-C5	3.212	3.459	3.452	3.488	4.087	3.532	4.331	3.435
	C2-C5	3.312	3.539	3.571	3.569	4.220	3.615	4.463	3.515
	$\Delta E_{in\text{-}out}$		-4.11		37.15		201.79		289.64
DFTB	C1-C5	3.054	3.474	3.508	3.477	4.078	3.485	4.258	3.555
	C2-C5	3.106	3.510	3.604	3.513	4.194	3.524	4.357	3.596
	$\Delta E_{in\text{-}out}$		-5.50		54.36		215.19		299.48
DFTB –Lennard Jones Dispersion	C1-C5	3.134	3.550	3.530	3.557	4.103	3.54	4.287	3.629
	C2-C5	3.193	3.596	3.627	3.602	4.219	3.586	4.385	3.677
	$\Delta E_{in\text{-}out}$		-4.45		51.14		213.83		295.85
LDA/ 6-31G(d)	C1-C5	3.005	3.441	3.485	3.436	3.911	3.470	4.081	3.460
	C2-C5	3.054	3.478	3.576	3.473	4.007	3.509	4.155	3.499
	$\Delta E_{in\text{-}out}$		-12.95		40.27		149.54		200.15

a- Nonbonded contacts are given in Å b- labelling of atoms is given in Figure 3 c- Relative energies between the two isomers $\Delta E_{in\text{-}out}$ in kcal/mol

Table S3. Comparison of calculated C3-C bond lengths[a,b] of in/out- [3⁴,¹⁰][7]metacyclophane and their fluorine, chlorine and bromine containing analogues

Method		*in*-H	*out*-H	*in*-F	*out*-F	*in*-Cl	*out*-Cl	*in*-Br	*out*-Br
HF/3-21G	C3-C	1.577	1.572	1.607	1.571	1.687	1.576	1.729	1.578
HF-D3/3-21G	C3-C	1.555	1.557	1.584	1.556	1.659	1.561	1.695	1.563
MP2/6-31G(d)	C3-C	1.560	1.556	1.588	1.556	1.651	1.561	1.698	1.562
MP2-D3/6-31G(d)	C3-C	1.539	1.541	1.567	1.541	1.651	1.547	1.656	1.547
LDA/6-31G(d)	C3-C	1.549	1.547	1.575	1.547	1.634	1.553	1.671	1.553
LDA/TZP	C3-C	1.545	1.544	1.572	1.544	1.634	1.548	1.679	1.548
BP86/6-31G(d)	C3-C	1.575	1.570	1.604	1.571	1.672	1.575	1.716	1.576
BP86-D3/6-31G(d)	C3-C	1.572	1.568	1.599	1.569	1.665	1.574	1.708	1.574
PBE-D3/TZP	C3-C	1.570	1.566	1.600	1.566	1.667	1.57	1.718	1.571
M06-L/TZP	C3-C	1.557	1.551	1.585	1.551	1.651	1.555	1.696	1.555
M06-2X/6-31G(d)	C3-C	1.563	1.557	1.591	1.557	1.652	1.563	1.687	1.564
B3LYP/6-31G(d)	C3-C	1.573	1.556	1.602	1.566	1.671	1.571	1.713	1.571
B3LYP-D3/6-31G(d)	C3-C	1.568	1.564	1.596	1.564	1.664	1.569	1.705	1.569
MMFF94	C3-C	1.568	1.550	1.587	1.551	1.661	1.553	1.964	1.856
DFTB	C3-C	1.566	1.560	1.595	1.560	1.700	1.564	1.776	1.567
DFTB –Lennard Jones Dispersion	C3-C	1.587	1.575	1.615	1.575	1.724	1.578	1.816	1.581

a- Bond lengths are given in Å b- labelling of atoms is given in Figure 3

Table S4. Comparison of calculated C3-S bond lengths[a,b] of in/out-2,6,15-trithia-[3⁴,¹⁰][7]metacyclophane and their fluorine, chlorine and bromine containing analogues

Method		*in*-H	*out*-H	*in*-F	*out*-F	*in*-Cl	*out*-Cl	*in*-Br	*out*-Br
HF/3-21G	C3-S	1.929	1.936	1.973	1.936	2.100	1.941	2.186	1.944
HF-D3/3-21G	C3-S	1.898	1.915	1.936	1.913	2.045	1.918	2.125	1.920
MP2/6-31G(d)	C3-S	1.848	1.854	1.882	1.854	1.969	1.860	2.060	1.861
MP2-D3/6-31G(d)	C3-S	1.822	1.834	1.850	1.834	1.922	1.840	1.992	1.840
LDA/6-31G(d)	C3-S	1.847	1.856	1.881	1.856	1.979	1.969	2.190	1.861
LDA/TZP	C3-S	1.838	1.848	1.872	1.847	1.977	1.851	-[c]	1.852
BP86/6-31G(d)	C3-S	1.885	1.890	1.928	1.891	2.066	1.895	2.692	1.896
BP86-D3/6-31G(d)	C3-S	1.879	1.886	1.918	1.887	2.045	1.892	2.622	1.893
PBE-D3/TZP	C3-S	1.874	1.880	1.915	1.880	2.045	1.884	-[c]	1.885
M06-L/TZP	C3-S	1.858	1.858	1.896	1.863	2.017	1.867	-[c]	1.868
M06-2X/6-31G(d)	C3-S	1.844	1.847	1.880	1.848	1.994	2.045	2.134	1.856
B3LYP/6-31G(d)	C3-S	1.881	1.884	1.924	1.884	2.056	1.889	2.467	1.890
B3LYP-D3/6-31G(d)	C3-S	1.874	1.880	1.914	1.880	2.037	1.885	2.513	1.886
MMFF94	C3-S	1.871	1.856	1.892	1.856	1.982	1.860	2.026	1.859
DFTB	C3-S	1.896	1.898	1.936	1.896	3.000	1.901	-[c]	1.903
DFTB –Lennard Jones Dispersion	C3-S	1.896	1.917	1.963	1.916	-[b]	1.921	-[c]	1.924

a- Bond lengths are given in Å b- labelling of atoms is given in Figure 3 c- Employed method failed to optimize these isomers

Table S5. EDA-NOCV Energy Decomposition Analysis[a] using PBE-D3/TZP//LDA/TZP level of theory on in/out- 2,6,15-trithia-[$3^{4,10}$][7]metacyclophane and its halogen substituted analogues as well as the x-ray crystallographic structure[b] of in/out- 2,6,15-trithia-[$3^{4,10}$][7]metacyclophane[7]

	X-ray[b] (VAMMEB)	*in*-H	*out*-H	*in*-F	*out*-F	*in*-Cl	*out*-Cl	*in*-Br[c]	*out*-Br
E_{Pauli}	178.84	188.90	128.79	408.32	288.99	499.83	200.45	-	167.95
E_{el}	-101.66	-103.69	-77.78	-168.61	-129.46	-235.03	-116.25	-	-106.56
E_{orb}	-172.55	-178.30	-152.41	-321.90	-280.62	-261.07	-168.65	-	-132.34
$E_{orb}^1(\Delta q)$[d]	-163.74 (0.94)	-168.81 (0.96)	-144.6 (0.95)	-280.85 (1.21)	-258.57 (1.21)	-190.31 (1.22)	-151.26 (1.17)	-	-118.88 (1.18)
$E_{orb}^2(\Delta q)$[d]	-	-	-	-12.68(0.24)	-7.56(0.19)	-16.35(0.39)	-5.21(0.16)	-	-3.76(0.14)
$E_{orb}^3(\Delta q)$[d]	-	-	-	-12.68(0.24)	-7.55(0.19)	-16.32(0.39)	-5.20(0.16)	-	-3.76(0.14)
E_{disp}	-1.17	-1.12	-0.55	-1.92	-1.00	-2.6	-1.92	-	-2.29
E_{int}	-96.54	-94.21	-101.95	-84.11	-122.09	1.13	-86.37	-	-73.24
E_{prep}	159.38	8.25	23.38	24.58	22.76	53.4	24.95	-	24.53

a- Energy components are given in kcal/mol b- CSD ref. code VAMMEB c- Employed methods failed to optimize *in*-bromine-- 2,6,15-trithia-[$3^{4,10}$][7]metacyclophane d- Orbital contribution is decomposed into individual contributions (E_{orb}^i) and combined for alpha and beta spin; the charge transfer through these channels, Δq, is indicated in parentheses

Table S6. EDA-NOCV Energy Decomposition Analysis[a] on M06-L/TZP and LDA/TZP geometries of in/out- 2,6,15-trithia-[$3^{4,10}$][7]metacyclophane, as well as the x-ray crystallographic structure[b] of in/out- 2,6,15-trithia-[$3^{4,10}$][7]metacyclophane[7] using M06-L/TZP

	X-ray[b] (VAMMEB)	*in*-H (LDA/TZP[c])	*out*-H (LDA/TZP[c])	*in*-H (M06-L/TZP[c])	*out*-H (M06-L/TZP[c])
E_{Pauli}	178.59	188.65	130.32	185.06	134.58
E_{el}	-100.49	-102.38	-79.08	-99.50	-80.09
E_{orb}	-174.48	-180.65	-154.47	-182.06	-157.2
$E_{orb}^1(\Delta q)$[d]	-166.38 (0.94)	-171.16 (0.96)	-145.84 (0.95)	-172.32 (0.95)	-148.43 (0.95)
$E_{orb}^2(\Delta q)$[d]	-	-	-	-	-
E_{int}	-96.38	-94.38	-103.23	-96.5	-102.7
E_{prep}	146.44	10.11	26.89	10.18	23.91

a- Energy components are given in kcal/mol b- CSD ref. code VAMMEB c- level of theory employed to obtain geometries. d- Orbital contribution is decomposed into individual contributions (E_{orb}^i) and combined for alpha and beta spin; the charge transfer through these channels, Δq, is indicated in parentheses

Table S7. EDA-NOCV Energy Decomposition Analysis[a] on M06-2X/TZP and LDA/TZP geometries of in/out- 2,6,15-trithia-[$3^{4,10}$][7]metacyclophane, as well as the x-ray crystallographic structure[b] of in/out- 2,6,15-trithia-[$3^{4,10}$][7]metacyclophane[7] using M06-2X/TZP

	X-ray[b] (VAMMEB)	*in*-H (LDA/TZP[c])	*out*-H (LDA/TZP[c])	*in*-H (M06-2X/TZP[c])	*out*-H (M06-2X/TZP[c])
E_{Pauli}	184.03	193.82	131.35	188.26	136.57
E_{el}	-107.54	-109.36	-78.65	-104.44	-79.43
E_{orb}	-179.61	-185.71	-162.38	-187.9	-165.87
$E_{orb}^1(\Delta q)$[d]	-168.25 (0.95)	-173.23 (0.96)	-151.78 (0.96)	-175.22 (0.95)	-155.30 (0.96)
$E_{orb}^2(\Delta q)$[d]	-	-	-	-	-
E_{int}	-103.12	-101.25	-109.68	-104.07	-108.74
E_{prep}	184.98	44.92	64.34	45.21	60.54

a- Energy components are given in kcal/mol b- CSD ref. code VAMMEB c- level of theory employed to obtain geometries d- Orbital contribution is decomposed into individual contributions (E_{orb}^i) and combined for alpha and beta spin; the charge transfer through these channels, Δq, is indicated in parentheses

Table S8. EDA-NOCV Energy Decomposition Analysis[a] on PBE-D3/QZ4P and LDA/TZP geometries of in/out- 2,6,15-trithia-[3[4,10]][7]metacyclophane, as well as the x-ray crystallographic structure[b] of in/out- 2,6,15-trithia-[3[4,10]][7]metacyclophane[7] using PBE-D3/QZ4P

	X-ray[b] (VAMMEB)	in-H (LDA/TZP[c])	out-H (LDA/TZP[c])	in-H (PBE-D3/QZ4P[c])	out-H (PBE-D3/QZ4P[c])
E_{Pauli}	179.25	189.22	128.68	180.08	127.35
E_{el}	-100.93	-102.45	-76.02	-97.94	-75.37
E_{orb}	-174.39	-180.57	-154.36	-179.14	-154.30
$E^1_{orb}(\Delta q)$[d]	-164.82 (0.95)	-170.05 (0.96)	-145.04 (0.95)	-169.08 (0.95)	-145.30 (0.95)
$E^2_{orb}(\Delta q)$[d]	-	-	-	-	-
E_{disp}	-1.17	-1.12	-0.55	-1.14	-0.52
E_{int}	-97.23	-94.91	-102.25	-98.14	-102.84
E_{prep}	156.68	8.00	23.32	8.84	21.6

a- Energy components are given in kcal/mol b- CSD ref. code VAMMEB c- level of theory employed to obtain geometries d- Orbital contribution is decomposed into individual contributions (E^i_{orb}) and combined for alpha and beta spin; the charge transfer through these channels, Δq, is indicated in parentheses

Table S9. Results of SAPT analysis[b] on model systems for [3[4,10]][7]metacyclophane and its halogen substituted analogues using aug-cc-pVTZ basis set for DF-SAPT2+3 calculations with aug-cc-PVTZ-JKFIT as auxiliary basis set for SCF density fitting computations and aug-cc-PVTZ-RI as auxiliary basis set for SAPT density fitting computations

Molecule	X-Ar (Å)[a]	$E_{electrostatic}$	$E_{exchange}$	$E_{induction}$	$E_{dispersion}$	$E_{total\ SAPT}$
out-H		-3.04	11.04	-1.03	-7.77	-0.80
in-F	1.89	-28.18	84.74	-4.15	-19.89	32.51
out-F		-2.94	9.94	-1.29	-7.52	-1.81
in-Cl	2.03	-80.33	192.71	-9.52	-38.44	64.42
out-Cl		-2.81	9.68	-1.36	-7.84	-2.34
in-Br	2.08	-108.41	244.47	-13.68	-43.71	78.67
out-Br		-2.93	9.96	-1.44	-8.13	-2.54

a- X-Ar - the distance between halogen atom and center of the aromatic ring; b- Energy components are given in kcal/mol

Table S10. Results of SAPT analysis[b] on model systems for 2,6,15-trithia-[3[4,10]][7]metacyclophane and its halogen substituted analogues using aug-cc-pVTZ basis set for DF-SAPT2+3 calculations with aug-cc-PVTZ-JKFIT as auxiliary basis set for SCF density fitting computations and aug-cc-PVTZ-RI as auxiliary basis set for SAPT density fitting computations

Molecule	X-Ar (Å)[a]	$E_{electrostatic}$	$E_{exchange}$	$E_{induction}$	$E_{dispersion}$	$E_{total\ SAPT}$
out-H		-1.47	5.29	-0.44	-5.43	-2.05
in-F	1.97	-20.87	64.20	-3.29	-16.11	23.93
out-F		-1.86	4.88	-0.63	-5.34	-2.94
in-Cl	2.11	-58.71	143.66	-8.04	-31.36	45.55
out-Cl		-1.76	4.67	-0.67	-5.55	-3.30
in-Br	2.17	-90.91	206.24	-11.53	-38.22	65.57
out-Br		-1.83	4.81	-0.70	-5.74	-3.46

a- X-Ar - the distance between halogen atom and center of the aromatic ring; b- Energy components are given in kcal/mol

Table S11. EDA-NOCV Energy Decomposition Analysis[a] on model system for [3[4,10]][7]metacyclophane and its halogen substituted analogues using PBE-D3/TZP level of theory

	in-H	out-H	in-F	out-F	in-Cl	out-Cl	in-Br	out-Br
E_{Pauli}	47.74	7.99	73.32	7.26	178.38	6.94	228.66	7.14
E_{el}	-19.65	-3.05	-27.22	-2.77	-73.76	-2.46	-99.93	-2.63
E_{orb}	-10.23	-2.65	-9.04	-3.37	-29.47	-3.22	-37.47	-3.29
$E^1_{orb}(\Delta q)$[b]	-3.31 (0.13)	-0.52 (0.05)	-2.77 (0.10)	-	-7.37 (0.23)	-0.51 (0.06)	-9.04 (0.26)	-
$E^2_{orb}(\Delta q)$[b]	-1.22 (0.08)	-0.49 (0.05)	-1.20 (0.07)	-	-4.31 (0.17)	-0.05 (0.05)	-5.57 (0.22)	-
$E^3_{orb}(\Delta q)$[b]	-1.22 (0.08)	-0.48 (0.05)	-1.19 (0.07)	-	-4.32 (0.17)	-0.05(0.05)	-5.57 (0.22)	-
E_{disp}	-4.04	-3.42	-4.36	-3.43	-4.09	-3.75	-3.85	-3.85
E_{int}	13.82	-1.12	32.7	-2.32	71.05	-2.49	-2.63	-2.63
E_{prep}	27.58	24.43	55.28	24.54	86.22	3.79	23.59	23.59

a- Energy components are given in kcal/mol b- Orbital contribution is decomposed into individual contributions (E^i_{orb}); the charge transfer through these channels, Δq, is indicated in parentheses.

Table S12. EDA-NOCV Energy Decomposition Analysis[a] on model system for 2,6,15-trithia-[3[4,10]][7]metacyclophane and its halogen substituted analogues using PBE-D3/TZP level of theory

	in-H	*out*-H	*in*-F	*out*-F	*in*-Cl	*out*-Cl	*in*-Br	*out*-Br
E_{Pauli}	36.13	3.28	53.99	3.04	128.53	2.82	-	2.91
E_{el}	-15.47	-1.55	-20.12	-1.77	-53.44	-1.53	-	-1.65
E_{orb}	-7.37	-1.24	-5.93	-1.78	-21.1	-1.67	-	-1.69
$E_{orb}^{1}(\Delta q)$[b]	-2.87 (0.12)	-	-2.23 (0.10)	-	-6.22 (0.22)	-	-	-0.39 (0.05)
$E_{orb}^{2}(\Delta q)$[b]	-0.86 (0.07)	-	-0.89 (0.06)	-	-3.22 (0.14)	-	-	-
$E_{orb}^{3}(\Delta q)$[b]	-0.85 (0.07)	-	-0.89 (0.06)	-	-3.22 (0.14)	-	-	-
E_{disp}	-3.85	-3.04	-4.03	-3.09	-4.02	-3.32	-	-3.40
E_{int}	9.44	-2.55	23.91	-3.6	49.97	-3.7	-	-3.83
E_{prep}	18.54	16.16	41.2	16.47	58.35	15.96	-	15.89

a- Energy components are given in kcal/mol b- Orbital contribution is decomposed into individual contributions (E_{orb}^{i}); the charge transfer through these channels, Δq, is indicated in parentheses.
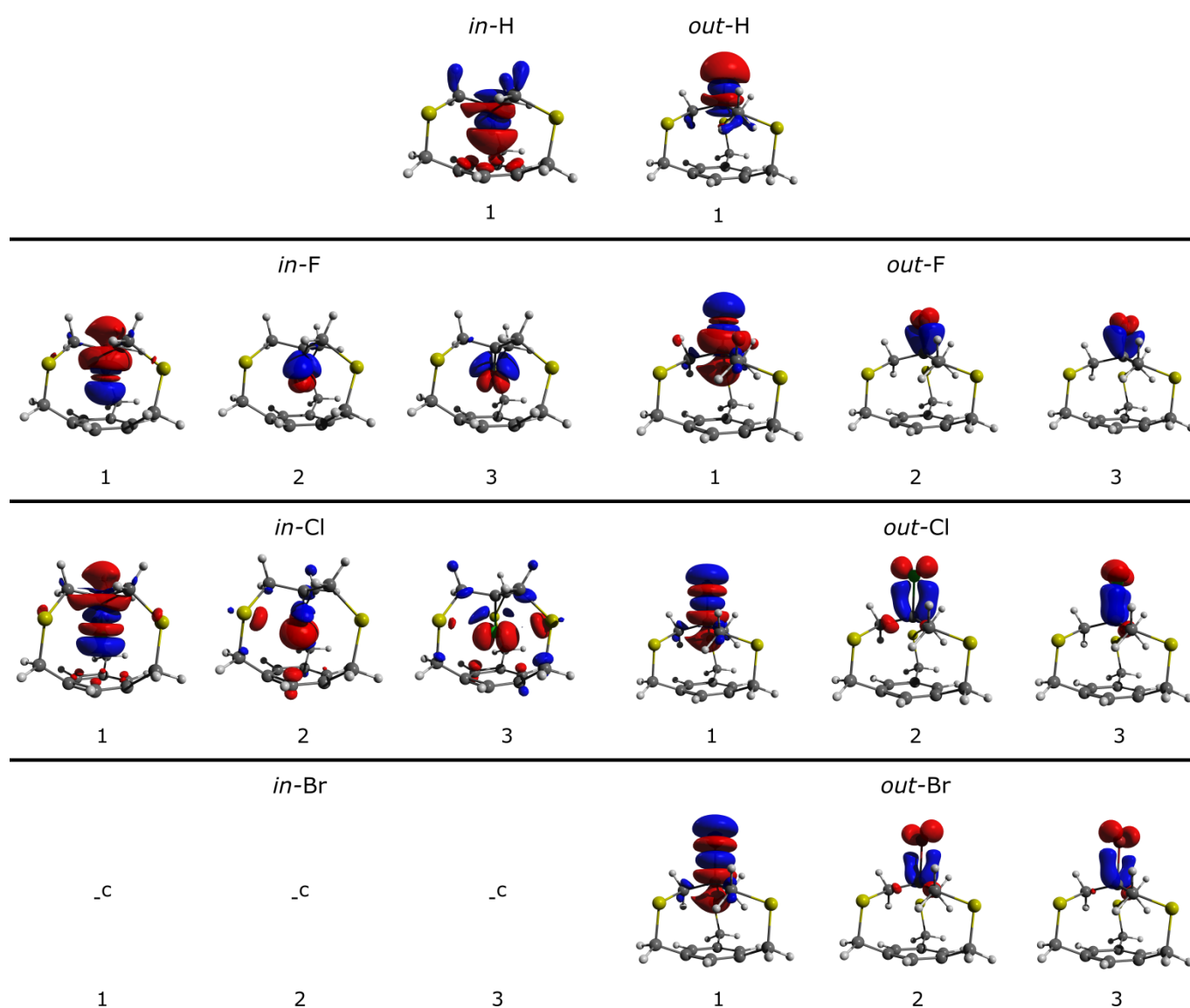
Figure S1. Most important contours of deformation density channels obtained via NOCV analysis using PBE-D3/TZP//LDA/TZP level of theory of 2,6,15-trithia-[3[4,10]][7]metacyclophane; electron flow is depicted from red to blue; isovalue 0.002au. The numbers correspond to the values of *i* in E_{orb}^{i}.
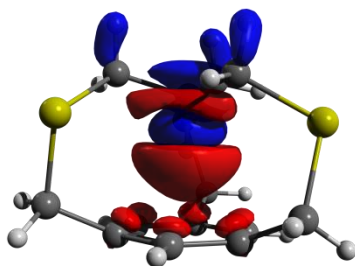
Figure S2. Most important contour of deformation density channels obtained via NOCV analysis on the X-ray structure employing PBE-D3/TZP, electron flow is depicted from red to blue; isovalue 0.002au, E^1_{orb}= -163.74 $\frac{kcal}{mol}$ Δq= 0.94

in-H

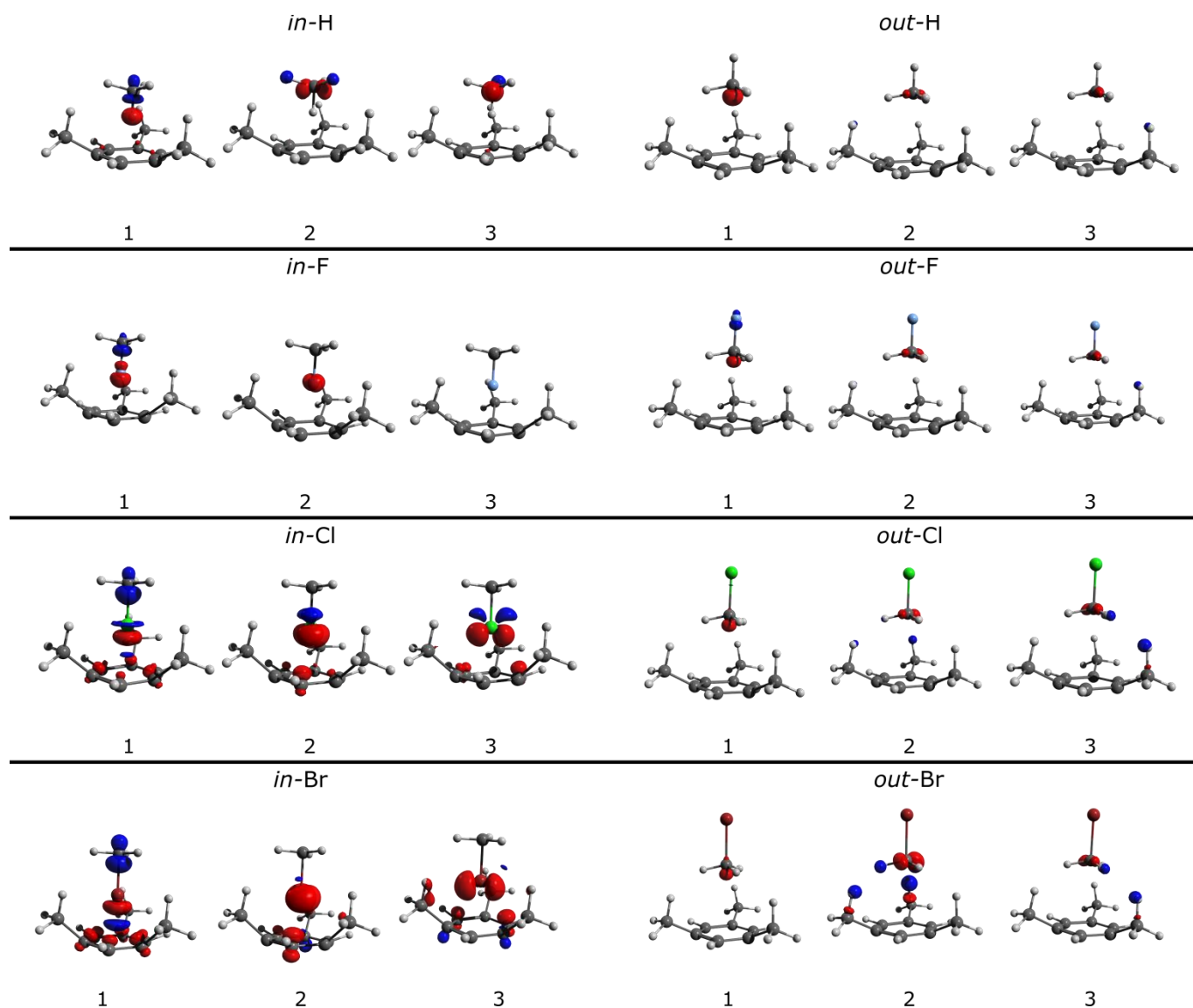*out*-H

| 1 | 2 | 3 | 1 | 2 | 3 |

in-F

out-F

| 1 | 2 | 3 | 1 | 2 | 3 |

in-Cl

out-Cl

| 1 | 2 | 3 | 1 | 2 | 3 |

in-Br

out-Br

| 1 | 2 | 3 | 1 | 2 | 3 |

Figure S3. Most important contours of deformation density channels obtained via NOCV analysis on the model system for [3⁴,¹⁰][7]metacyclophane and its halogen substituted analogues using PBE-D3/TZP; electron flow is depicted from red to blue; isovalue 0.002au. The numbers correspond to the values of *i* in E^i_{orb}.
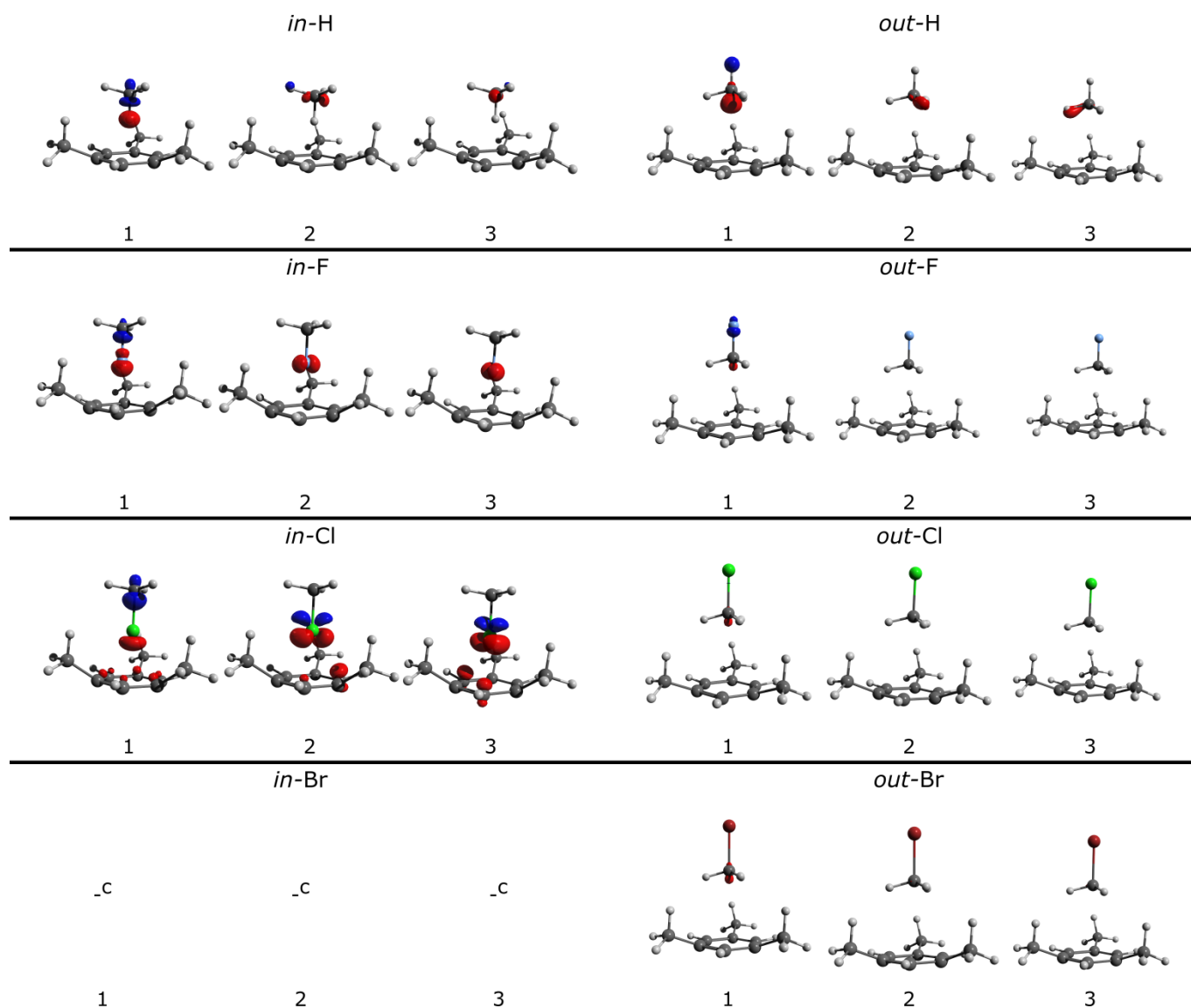
Figure S4. Most important contours of deformation density channels obtained via NOCV analysis on the model system for 2,6,15-trithia-[3^{4,10}][7]metacyclophane and its halogen substituted analogues using PBE-D3/TZP; electron flow is depicted from red to blue; isovalue 0.002au. The numbers correspond to the values of i in E_{orb}.

PCCP

Supplementary information

References

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