

Supplementary Information

Antiaromaticity-aromaticity transition of cyclo[16]carbon upon metal encapsulation

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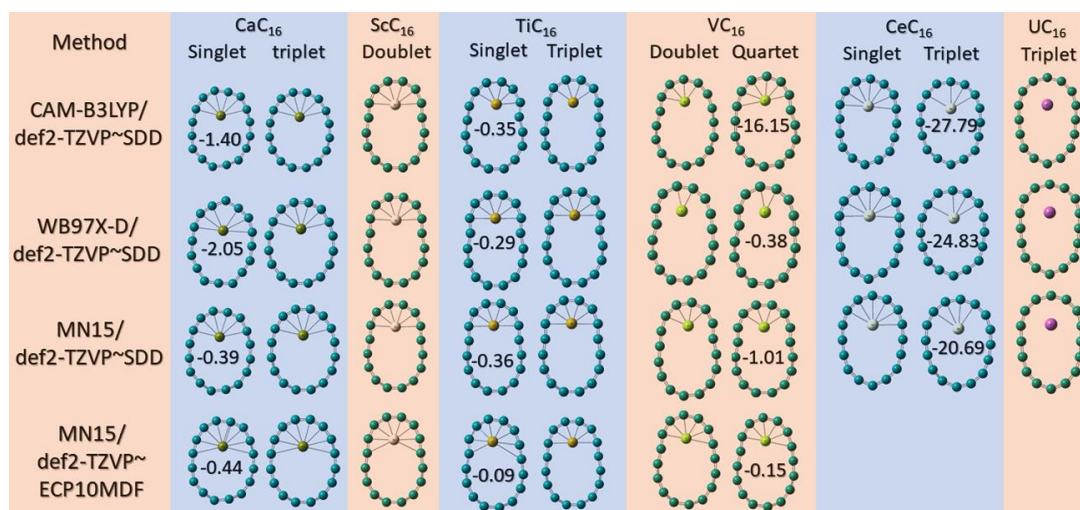


Figure S1. The optimized geometric structures of CaC_{16} , ScC_{16} , TiC_{16} , VC_{16} , CeC_{16} and UC_{16} at different theory levels. The def2-TZVP basis set was used for C, Ca, Sc, Ti and V atoms. The SDD basis sets, i.e. ECP28MWB and ECP60MWB, were used for Ce and U atoms, respectively. In addition, ECP10MDF was also employed for Ca, Sc, Ti and V atoms to evaluate the relativistic effects. The energy difference between the structures with different multiplicities is given in kcal/mol.

Table S1. Theoretically calculated binding energy (ΔE_b , in kcal/mol) of CaC_{16} , ScC_{16} , TiC_{16} , VC_{16} , CeC_{16} and UC_{16} by using different functionals. The def2-TZVP basis set was used for C, Ca, Sc, Ti and V atoms. The SDD basis sets, i.e. ECP28MWB and ECP60MWB, were used for Ce and U atoms, respectively. In addition, ECP10MDF was also employed for Ca, Sc, Ti and V atoms to evaluate the relativistic effects.

Methods	MN15	MN15	CAM-B3LYP	wB97X-D
	(ECP10MDF)			
CaC₁₆	-63.63	-59.36	-57.15	-65.42
ScC₁₆	-63.23	-95.57	-82.84	-93.32
TiC₁₆	-97.36	-129.05	-81.06	-90.45
VC₁₆	-86.02	-96.58	-57.69	-67.24
CeC₁₆	-67.29	-	-134.12	-147.27
UC₁₆	-118.15	-	-129.24	-129.64

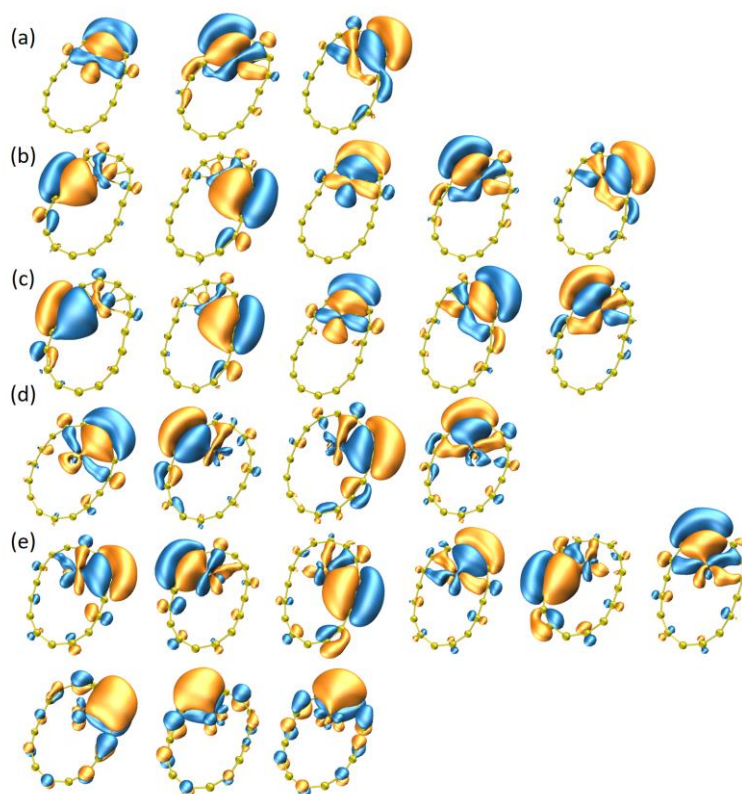


Figure S2. The isosurface map of localized molecular orbitals (LMOs) of (a) ScC_{16} , (b) TiC_{16} , (c) VC_{16} , (d) CeC_{16} and (e) UC_{16} . Only those LMOs with obvious overlap between metal and carbon atoms were listed for clarity.

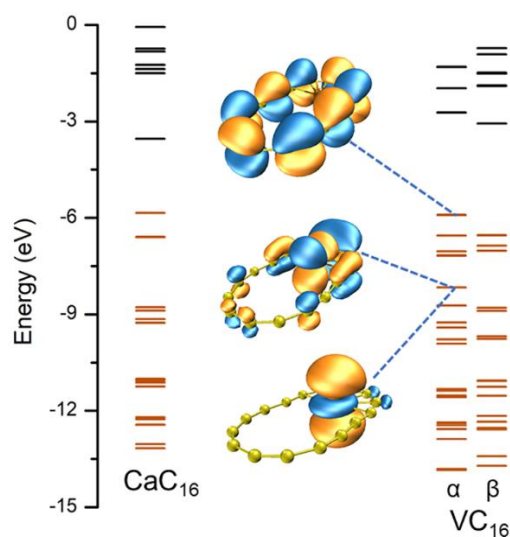


Figure S3. The energy diagram of CaC_{16} and VC_{16} . The energy level of the occupied and unoccupied CMOs are denoted in red and black, respectively. The molecular orbitals shown in the left of the energy diagram correspond to the unpaired electrons.

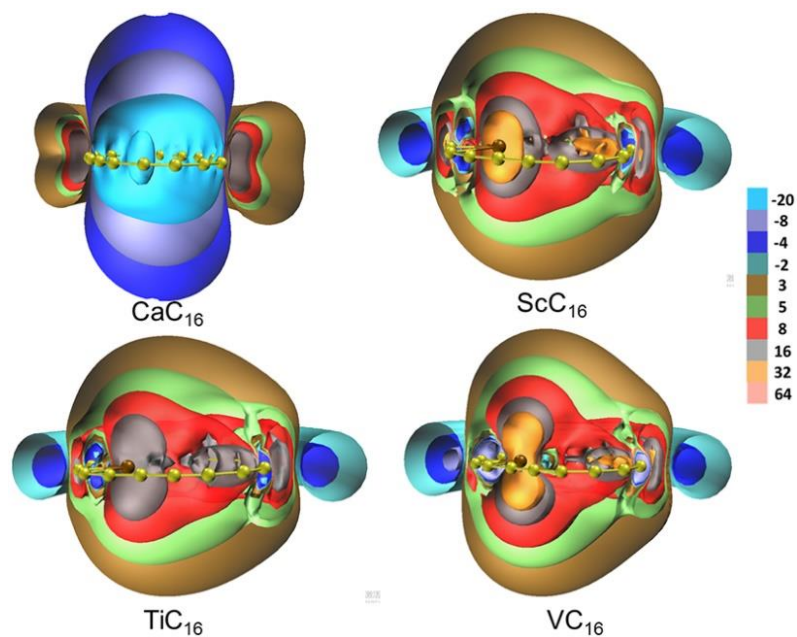


Figure S4. Multiple clipped isosurfaces of ICSS_{zz} of MC₁₆ (M = Ca, Ti, Sc, V) calculated at MN15/def2-TZVP~ECP10MDF level of theory.

Table S2. The magnetically induced current intensities (in nA/T) passing through each C-C bond in MC₁₆ (M = Ca, Ti, Sc, V, Ce, U) calculated by using the MN15 functional. The def2-TZVP basis set was used for C, Ca, Sc, Ti and V atoms. The SDD basis sets, i.e. ECP28MWB and ECP60MWB, were used for Ce and U atoms, respectively. Note that “R” represents that the data were obtained at MN15/def2-TZVP~ECP10MDF level of theory.

Bond	CaC₁₆		ScC₁₆		TiC₁₆		VC₁₆		CeC₁₆	UC₁₆
Index	-	R	-	R	-	R	-	R	-	-
1	-25.33	-24.1	6.47	7.13	9.60	8.62	9.15	7.46	2.75	59.68
2	-24.49	-23.34	8.76	8.85	10.34	9.88	11.41	9.23	3.96	58.47
3	-24.51	-23.32	9.17	9.36	10.15	10.07	13.16	12.35	5.11	59.66
4	-25.25	-23.9	8.22	8.62	10.36	10.91	13.79	13.48	5.04	58.90
5	-25.78	-24.47	8.99	9.27	10.00	10.09	12.68	12.44	4.68	58.9

6	-25.66	-24.33	8.29	8.67	10.22	9.88	11.33	12.25	5.06	59.68
7	-24.78	-23.33	9.16	9.34	9.68	8.65	9.09	9.29	5.02	58.39
8	-25.10	-23.93	8.79	8.86	6.86	6.92	6.38	6.35	4.74	59.72
9	-25.82	-24.59	6.45	7.12	8.42	8.04	7.33	7.70	3.77	61.87
10	-25.11	-24.18	7.79	8.89	8.50	8.64	7.76	8.24	2.75	64.07
11	-24.88	-23.36	8.48	9.19	7.76	7.82	7.04	8.06	3.46	64.3
12	-24.60	-24.25	7.61	8.29	8.36	8.46	7.69	8.2	3.72	64.52
13	-24.91	-23.84	8.20	8.89	7.76	7.84	7.06	7.95	3.36	64.46
14	-25.10	-24.66	7.51	8.31	8.50	8.65	7.77	8.36	3.82	64.31
15	-24.80	-23.47	8.48	9.19	7.82	7.88	7.18	7.72	3.51	63.99
16	-25.31	-23.80	7.57	8.24	6.56	6.62	6.38	7.33	3.10	61.74

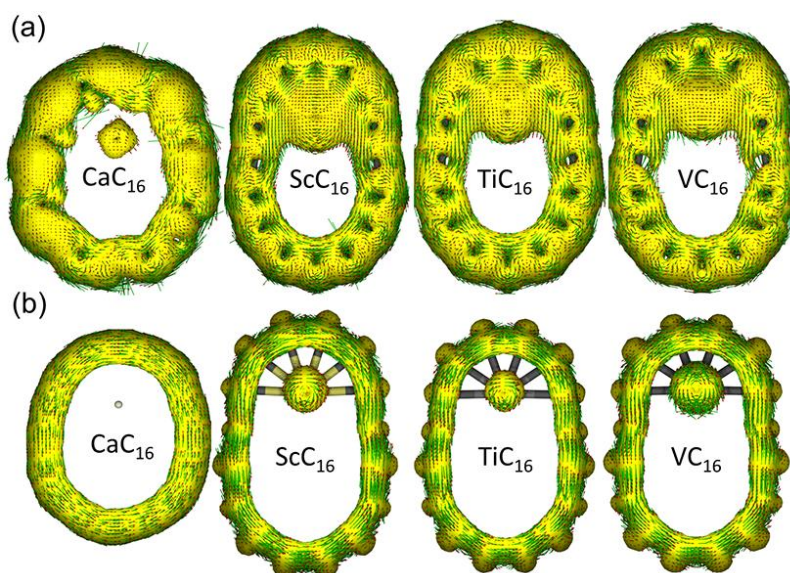
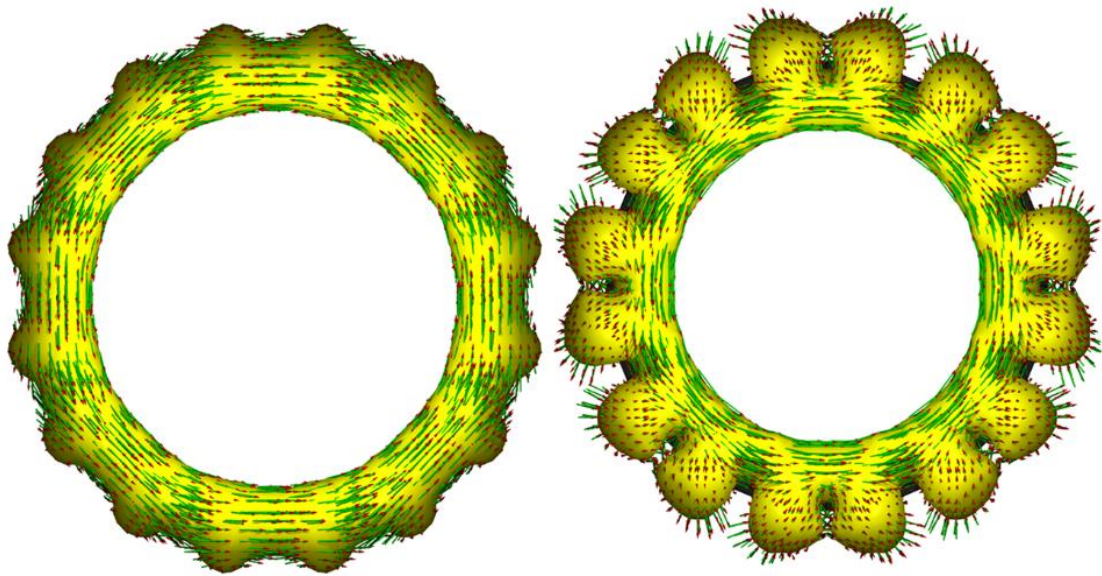


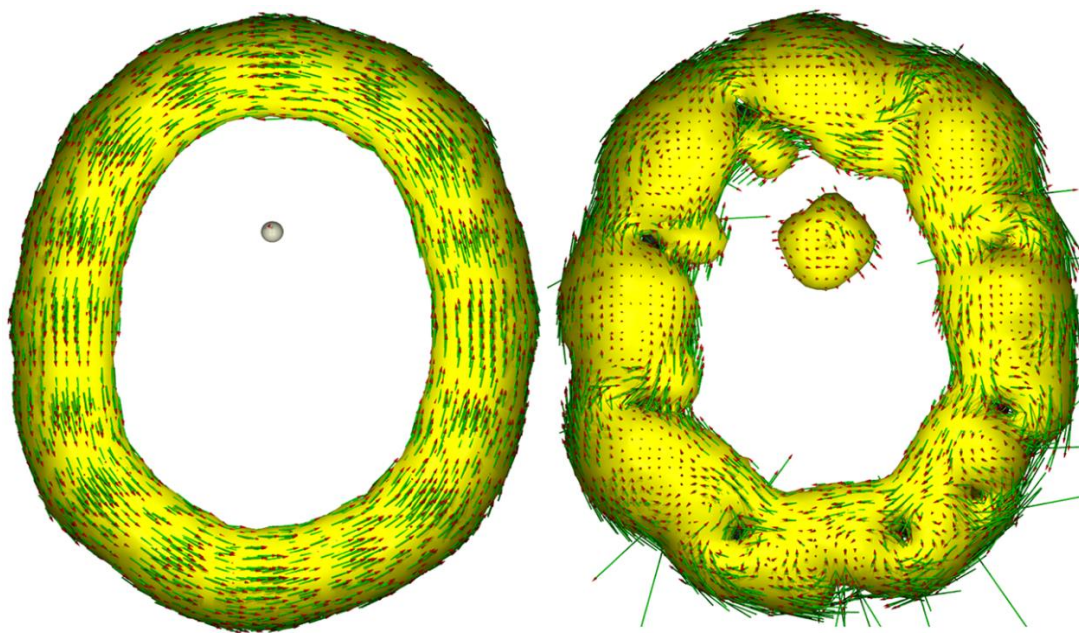
Figure S5. Anisotropy of the current-induced density (ACID) isosurface of MC_{16} ($M = Ca, Ti, Sc, V$) contributed by (a) π_{in} and (b) π_{out} orbitals calculated at MN15/def2-TZVP~ECP10MDF level of theory.

High-Resolution ACID plots:

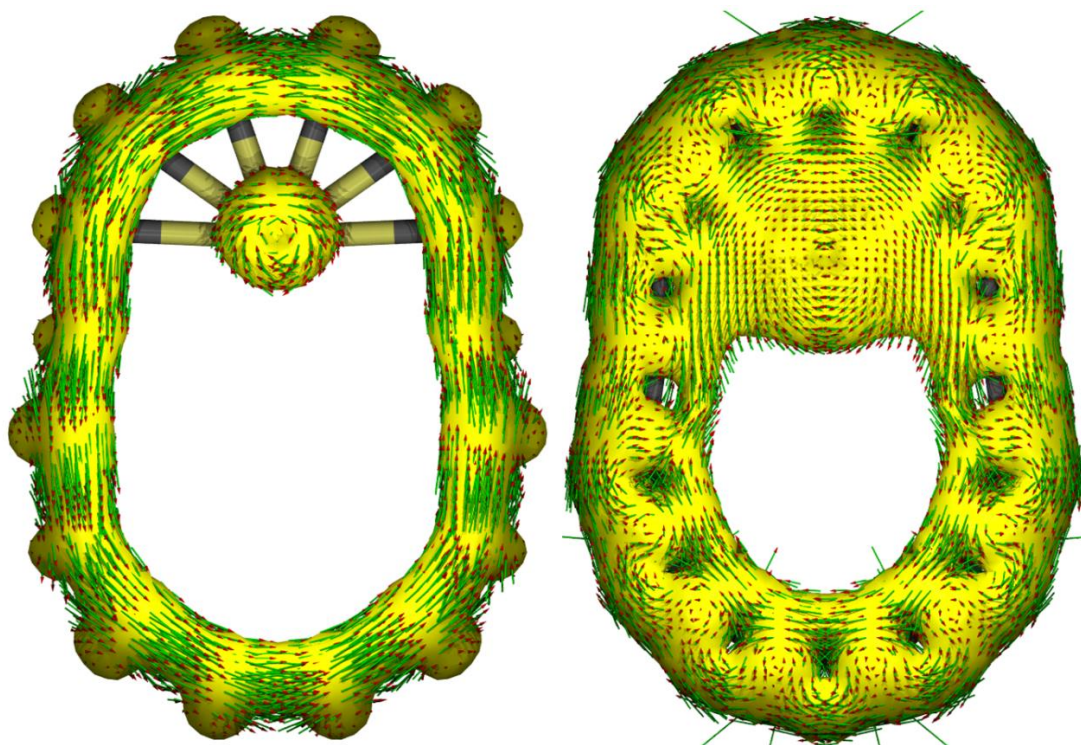
C_{16} :



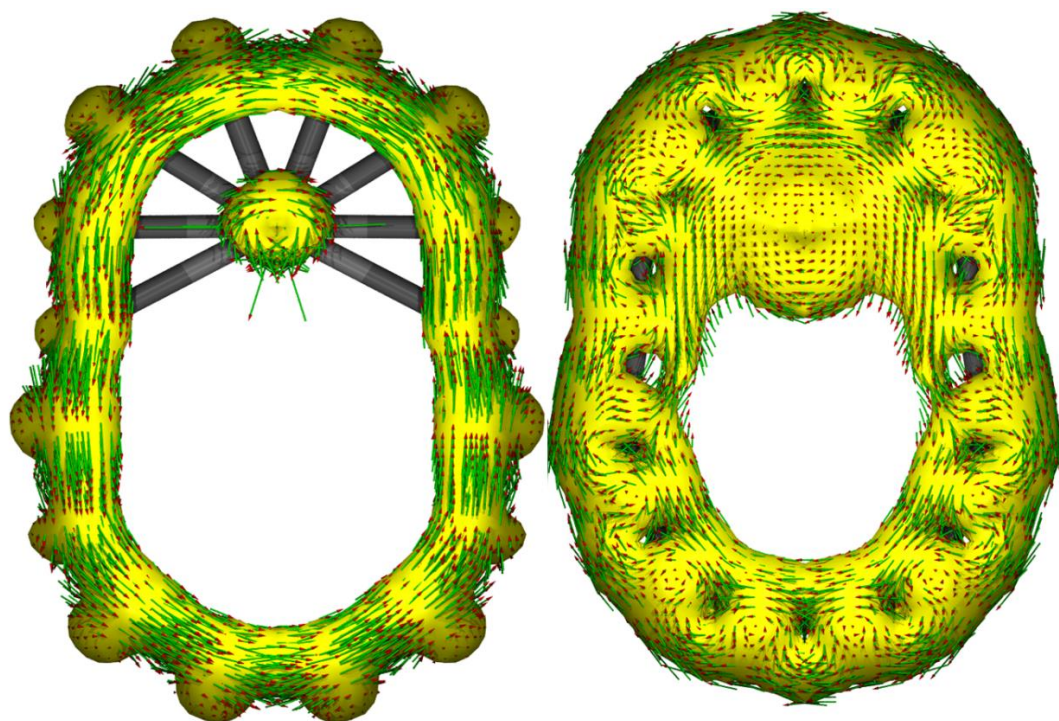
CaC_{16} :



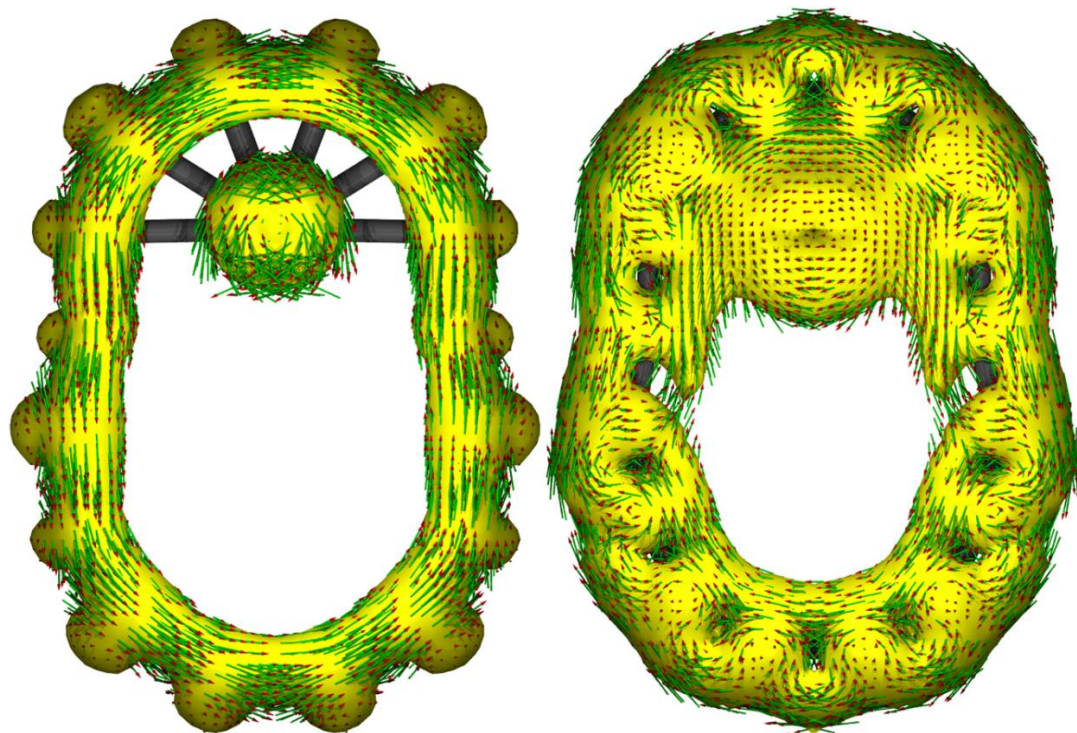
ScC₁₆:



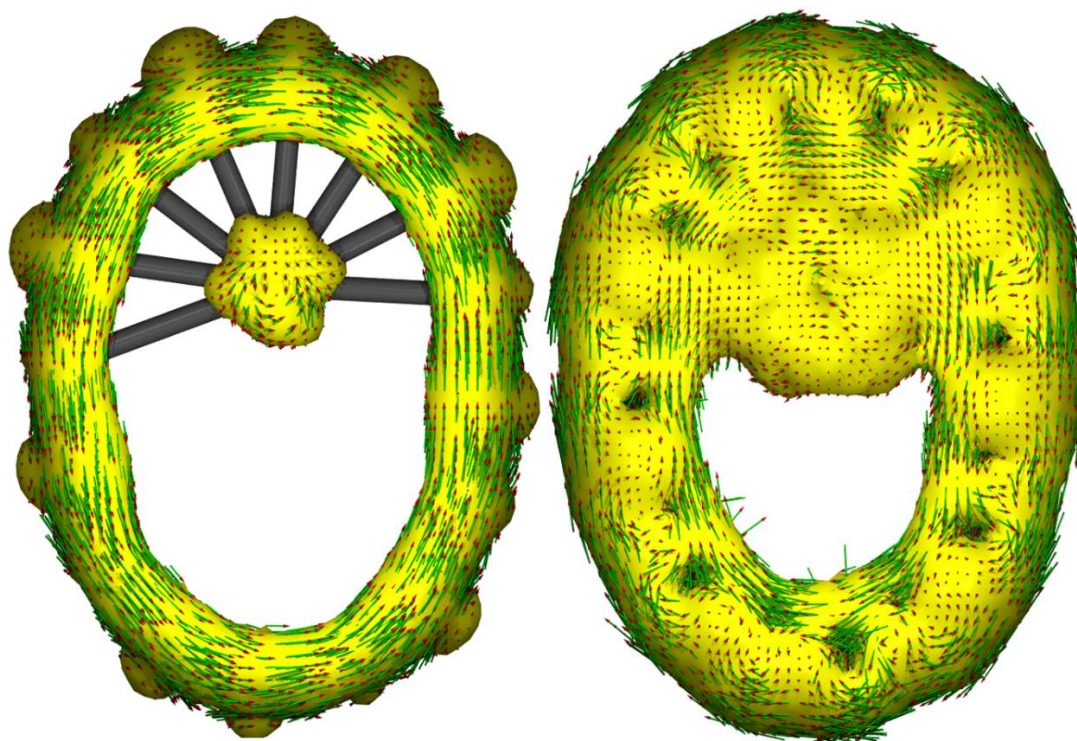
TiC₁₆:



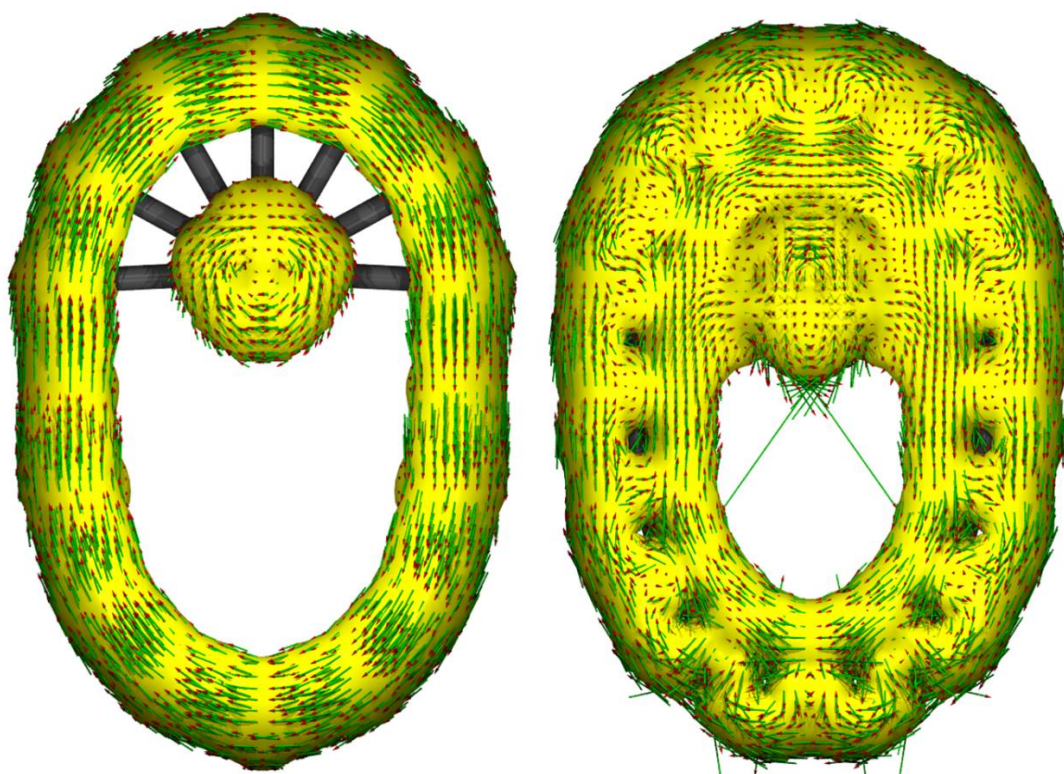
VC₁₆:



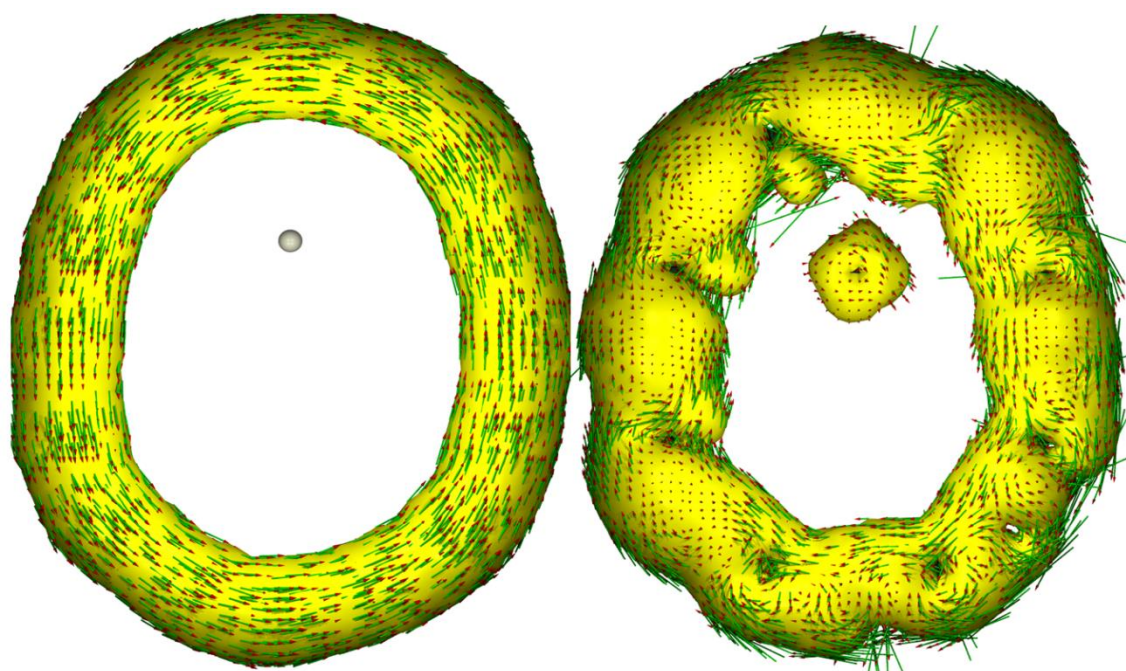
CeC₁₆:



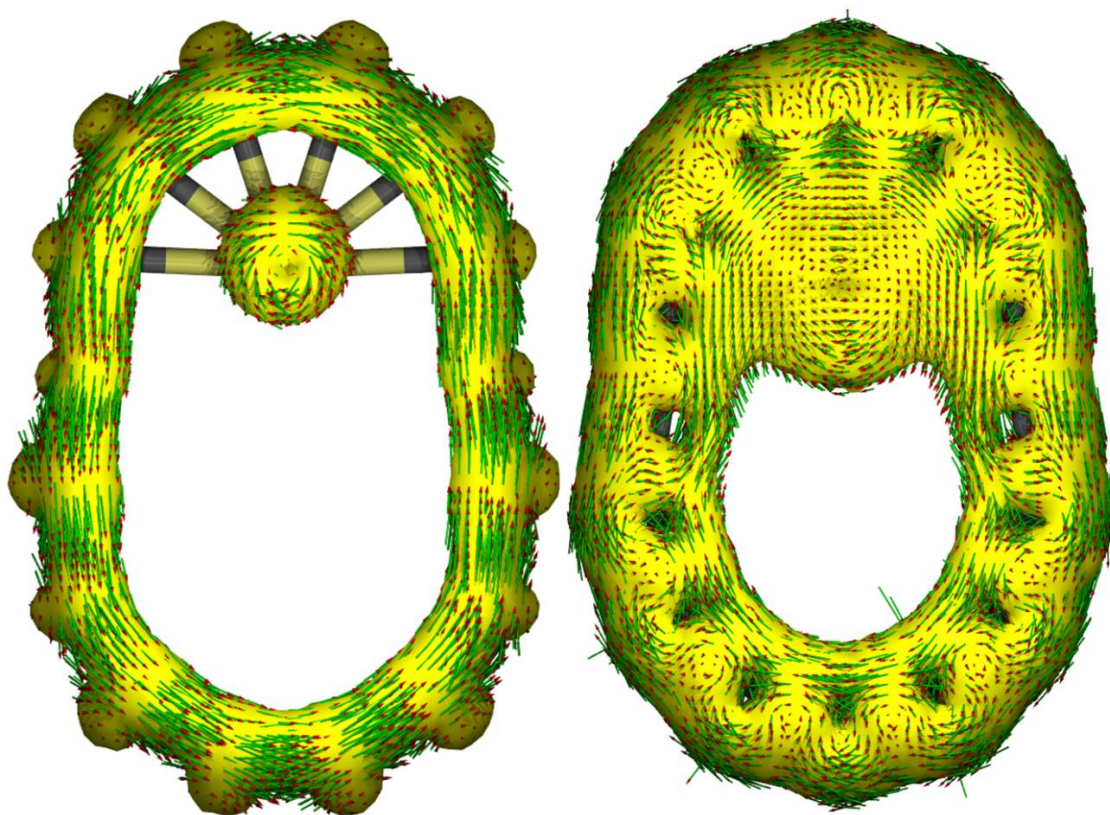
UC₁₆:



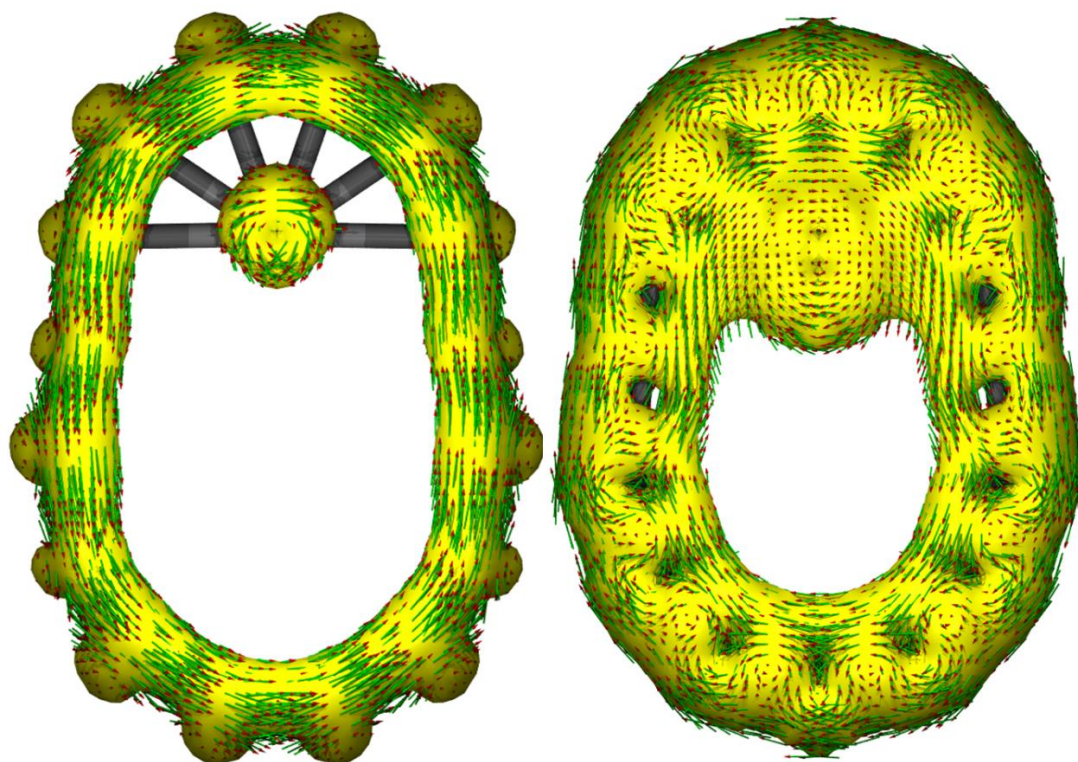
CaC₁₆: (ECP10MDF basis set for Ca)



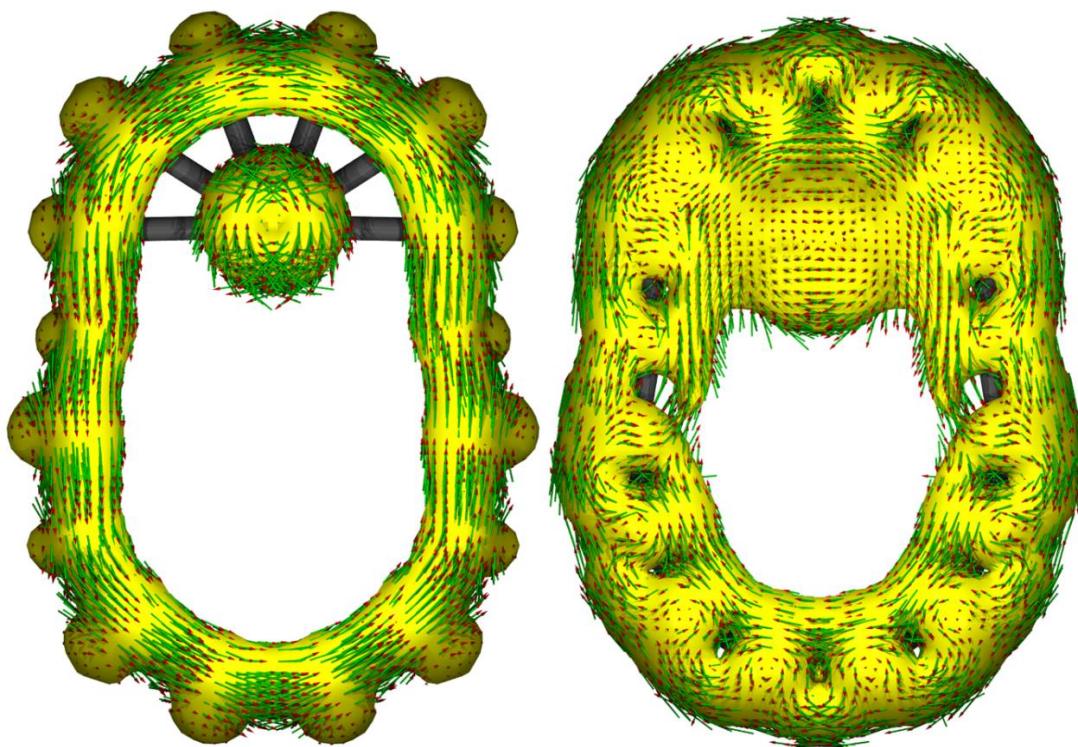
ScC₁₆: (ECP10MDF basis set for Sc)



TiC₁₆: (ECP10MDF basis set for Ti)



VC₁₆: (ECP10MDF basis set for V)



Cartesian Coordinates (Angstrom) of DFT-Optimized Structures:

Cyclo[16]carbon (in MN15/def2-TZVP level of theory)

0 1

C	0.60964800	3.25596700	0.00000000
C	1.87123000	2.73340200	0.00000000
C	2.73340200	1.87123000	0.00000000
C	3.25596700	0.60964800	0.00000000
C	3.25596700	-0.60964800	0.00000000
C	2.73340200	-1.87123000	0.00000000
C	1.87123000	-2.73340200	0.00000000
C	0.60964800	-3.25596700	0.00000000
C	-0.60964800	-3.25596700	0.00000000
C	-1.87123000	-2.73340200	0.00000000
C	-2.73340200	-1.87123000	0.00000000
C	-0.60964800	3.25596700	0.00000000
C	-2.73340200	1.87123000	0.00000000
C	-1.87123000	2.73340200	0.00000000
C	-3.25596700	-0.60964800	0.00000000
C	-3.25596700	0.60964800	0.00000000

CaC₁₆ singlet (in MN15/def2-TZVP level of theory)

0 1

C	-2.78158000	-0.87086400	0.00000000
C	-2.72498800	0.44414500	0.00000000
C	-2.40676400	1.67832200	0.00000000
C	-1.71825200	2.79804900	0.00000000
C	-0.59580500	3.42957200	0.00000000
C	0.72371600	3.31858400	0.00000000
C	1.89172600	2.81572600	0.00000000
C	2.49468500	1.60068100	0.00000000
C	2.79052900	0.39398000	0.00000000
C	2.81469600	-0.95969900	0.00000000
C	2.47327700	-2.14183500	0.00000000
C	-2.66525000	-2.12562300	0.00000000
C	-0.77709200	-3.85092900	0.00000000
C	-1.79022000	-3.12886700	0.00000000
C	1.70446100	-3.25589000	0.00000000
C	0.56685900	-3.73011300	0.00000000
Ca	0.00000000	1.07542800	0.00000000

CaC₁₆ triplet (in MN15/def2-TZVP level of theory)

0 3

C	-2.82900500	-0.92476600	0.00000000
C	-2.79009200	0.40439100	0.00000000
C	-2.50111600	1.63463800	0.00000000
C	-1.79732800	2.75526900	0.00000000
C	-0.68058600	3.37997700	0.00000000
C	0.63613700	3.39340100	0.00000000
C	1.76330200	2.78707900	0.00000000
C	2.48519500	1.67858300	0.00000000
C	2.78654200	0.45074600	0.00000000
C	2.83338300	-0.87774600	0.00000000
C	2.54794500	-2.09049500	0.00000000
C	-2.53159500	-2.13413500	0.00000000
C	-0.65001800	-3.79603300	0.00000000
C	-1.74164400	-3.21434100	0.00000000
C	1.77512300	-3.18252000	0.00000000
C	0.69375800	-3.78342200	0.00000000
Ca	0.00000000	1.05581200	0.00000000

ScC₁₆ (in MN15/def2-TZVP level of theory)

0 2

C	-1.01614200	-2.50927000	0.00005300
C	0.29990100	-2.31636600	-0.00000800
C	1.57781900	-2.27087400	-0.00002700
C	2.79842100	-1.76090000	-0.00002400
C	3.49560600	-0.65869100	-0.00001200
C	3.49524000	0.65952100	0.00002200
C	2.79776700	1.76149600	0.00003200
C	1.57694500	2.27102400	0.00001700
C	0.29913100	2.31698600	-0.00000700
C	-1.01697300	2.50934300	-0.00007600
C	-2.25411600	2.37575700	0.00002300
C	-2.25332900	-2.37602700	-0.00001000
C	-4.07532300	-0.66836700	0.00001700
C	-3.40669500	-1.71333700	0.00000400
C	-3.40730600	1.71274500	0.00002100
C	-4.07549600	0.66749900	0.00002000
Sc	1.47558600	-0.00015400	-0.00001300

TiC₁₆ singlet (in UMN15/def2-TZVP level of theory)

0 1

C	-0.26849700	2.20141700	0.00299700
C	-1.54394100	2.20743400	-0.00152700
C	-2.78133100	1.73870200	-0.00399400
C	-3.50822200	0.65985600	-0.00311600
C	-3.50790700	-0.66041000	-0.00338800
C	-2.78082600	-1.73900500	-0.00196800
C	-1.54331700	-2.20768700	0.00133500
C	-0.26804100	-2.20262300	0.00487900
C	1.04796800	-2.40423100	0.00078700
C	2.28487800	-2.30013800	-0.00073000
C	3.47050300	-1.69406600	-0.00223400
C	1.04732400	2.40432900	0.00279600
C	3.46980600	1.69434800	-0.00036500
C	2.28429800	2.30047300	0.00157200
C	4.16534400	-0.66806300	-0.00297000
C	4.16545600	0.66886900	-0.00219900
Ti	-1.56368100	0.00021700	0.00221600

TiC₁₆ triplet (in MN15/def2-TZVP level of theory)

0 3

C	-2.21285900	0.26753800	0.00000000
C	-2.21007700	1.54282500	0.00000000
C	-1.73911400	2.77941000	0.00000000
C	-0.66048900	3.50595400	0.00000000
C	0.66054200	3.50593600	0.00000000
C	1.73914500	2.77936000	0.00000000
C	2.21007500	1.54276100	0.00000000
C	2.21280700	0.26747600	0.00000000
C	2.41307700	-1.04793600	0.00000000
C	2.30462500	-2.28499100	0.00000000
C	1.69600500	-3.46860100	0.00000000
C	-2.41305200	-1.04788700	0.00000000
C	-1.69601900	-3.46855900	0.00000000
C	-2.30462700	-2.28494500	0.00000000
C	0.66811100	-4.16145500	0.00000000
C	-0.66814900	-4.16145200	0.00000000
Ti	0.00000000	1.56397200	0.00000000

VC₁₆ doublet (in MN15/def2-TZVP level of theory)

0 2

C	2.61286000	-2.19716200	0.00046200
C	1.39868200	-2.45971700	0.00025800

C	0.07882400	-2.36523500	-0.00003900
C	-1.17651800	-2.24468800	-0.00028700
C	-2.44981400	-1.87883600	-0.00055600
C	-3.36132300	-0.96589200	-0.00073400
C	-3.57081200	0.34276300	-0.00074300
C	-2.99641800	1.51416700	-0.00053300
C	-1.82203600	2.11717100	-0.00017500
C	-0.53791300	2.13810100	0.00018500
C	0.76224100	2.41017800	0.00039100
C	3.73166500	-1.47911800	0.00062600
C	4.08082300	0.98601900	0.00056400
C	4.22166200	-0.33837100	0.00062700
C	2.00701300	2.40236300	0.00043000
C	3.23044800	1.89283800	0.00049000
V	-1.61983900	0.03271800	-0.00025100

VC₁₆ quartet (in MN15/def2-TZVP level of theory)

0 4

C	-2.16917900	0.24733700	0.00000000
C	-2.16772100	1.52081700	0.00000000
C	-1.71025100	2.76400600	0.00000000
C	-0.65884200	3.52296600	0.00000000
C	0.65809700	3.52329200	0.00000000
C	1.70981200	2.76475500	0.00000000
C	2.16745600	1.52164300	0.00000000
C	2.16884800	0.24812200	0.00000000
C	2.37121300	-1.06544200	0.00000000
C	2.27498000	-2.30347900	0.00000000
C	1.68931100	-3.49762600	0.00000000
C	-2.37130200	-1.06626000	0.00000000
C	-1.68877200	-3.49833000	0.00000000
C	-2.27461600	-2.30425200	0.00000000
C	0.66810200	-4.20121800	0.00000000
C	-0.66713800	-4.20129300	0.00000000
V	0.00000000	1.57172900	0.00000000

CeC₁₆ singlet (in MN15/def2-TZVP ~ ECP28MWB level of theory)

0 1

C	1.68869939	2.47696339	-0.00006073
C	0.41012226	2.61492330	0.00025965
C	-0.88095500	2.54437509	0.00032361
C	-2.12161861	2.15856546	0.00023934

C	-2.97740324	1.18366337	0.00000546
C	-3.29897583	-0.07546433	-0.00010621
C	-2.90416947	-1.31465230	-0.00037708
C	-1.98465841	-2.22478883	-0.00009745
C	-0.73159034	-2.58775443	-0.00012043
C	0.55082436	-2.59721106	0.00021360
C	1.84034724	-2.44544401	0.00026820
C	2.93111450	2.13879548	-0.00042228
C	4.38931636	0.07312308	-0.00036322
C	3.84368029	1.24567311	-0.00051538
C	3.05709589	-2.07018387	0.00015171
C	3.93260748	-1.11990837	-0.00015914
Ce	-0.80114864	-0.00006984	0.00007866

CeC₁₆ triplet (in MN15/def2-TZVP ~ ECP28MWB level of theory)

0 3

C	-1.65626700	2.57428600	-0.00027200
C	-0.41821600	2.79540000	-0.00049800
C	0.90190800	2.75640300	-0.00054800
C	2.07454700	2.25567600	-0.00067100
C	2.96390400	1.28924900	-0.00074700
C	3.22910400	0.02500600	-0.00074700
C	2.88250700	-1.23577800	-0.00074500
C	2.01089000	-2.18436900	-0.00066300
C	0.77898600	-2.63441400	-0.00057600
C	-0.48828600	-2.72079400	-0.00047100
C	-1.79818900	-2.59727200	-0.00035400
C	-2.88127700	2.07429300	-0.00023000
C	-4.23964100	-0.03181100	-0.00014200
C	-3.78427900	1.21433200	-0.00014800
C	-2.98499700	-2.19018500	-0.00026100
C	-3.89294300	-1.23100600	-0.00017500
Ce	0.73132400	0.07696100	-0.00048900

UC₁₆ (in MN15/def2-TZVP ~ ECP60MWB level of theory)

0 3

C	-2.47707300	-0.65472000	0.00000000
C	-2.51824000	0.63911500	0.00000000
C	-2.17240500	1.88810000	0.00000000
C	-1.26054300	2.81892400	0.00000000
C	0.00028300	3.14901800	0.00000000
C	1.26105500	2.81872500	0.00000000

C	2.17277000	1.88775800	0.00000000
C	2.51841300	0.63871900	0.00000000
C	2.47704900	-0.65510700	0.00000000
C	2.37615300	-1.93962100	0.00000000
C	2.04069400	-3.17631200	0.00000000
C	-2.37634400	-1.93924500	0.00000000
C	-1.19599300	-4.13887600	0.00000000
C	-2.04107200	-3.17599000	0.00000000
C	1.19546200	-4.13906900	0.00000000
C	-0.00030100	-4.60503100	0.00000000
U	0.00009100	0.76126900	0.00000000