Electronic Supplementary Information

Highly oxidized U(VI) within the smallest fullerene: Gas-phase synthesis and computational study of boron-doped U@C_{27}B

Antonio Moreno-Vicente,[a] Marc Alías,[a] Paul W. Dunk,[b] Coen de Graaf,*[a,c] Josep M. Poblet[a] and Antonio Rodríguez-Fortea*[a]

[a.] *Departament Química Física i Inorgànica, Universitat Rovira i Virgili, C/Marcel·lí Domingo 1, 43007, Tarragona, Spain.*
[b.] *National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, FL 32310, USA.*
[c.] *ICREA, Pg Lluis Companys 23, 08010, Barcelona, Spain.*

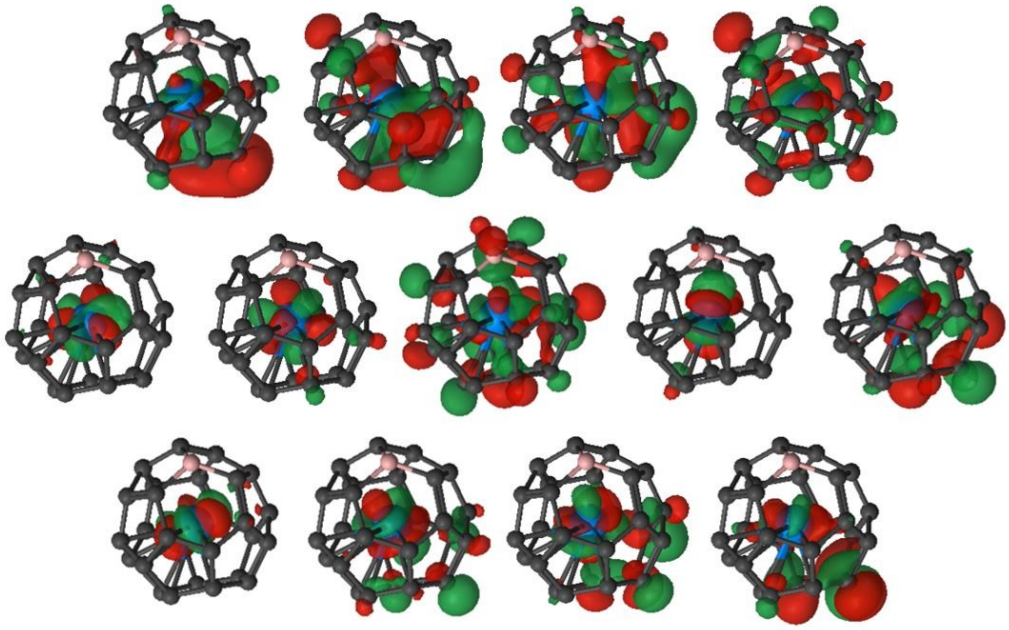


Figure S1. SA(10)-CASSCF natural orbitals for the 10 lowest doublets in U@C_{27}B.

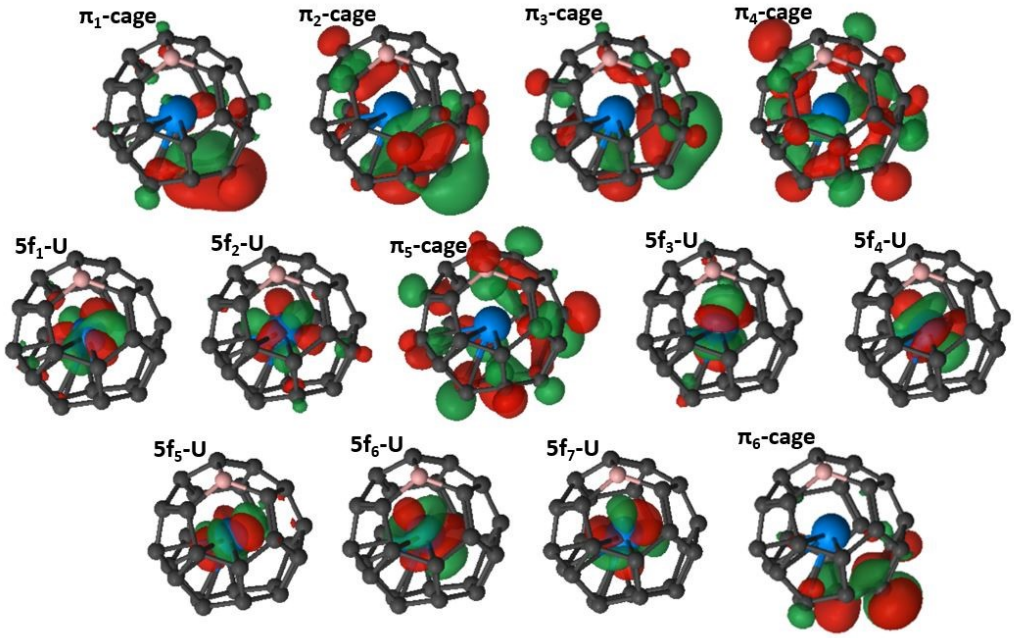


Figure S2. CASSCF localized orbitals for the 10 lowest doublets in U@C_{27}B.

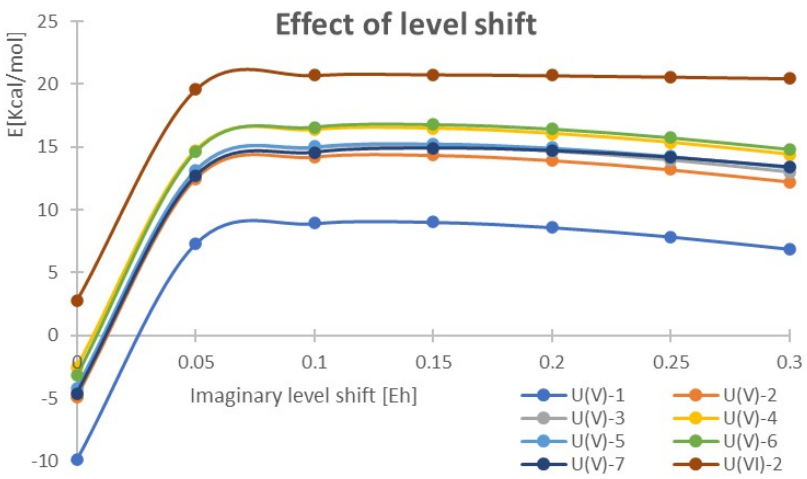
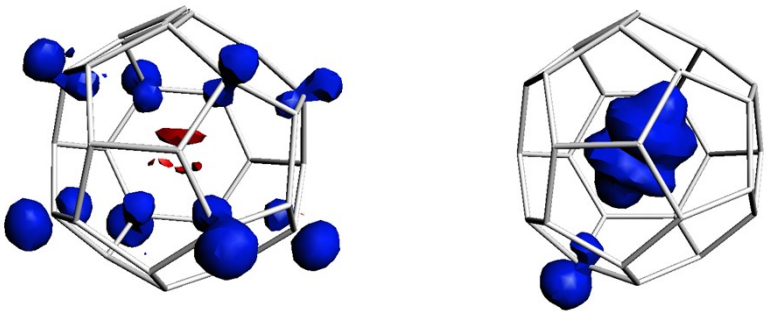


Figure S3. Effect of the imaginary level shift in the CASPT2 relative energies. The zero of energy at each imaginary level shift is established by the energy of the U(VI)-1 state.



(a) (b)

Figure S4. Spin density (0.007 a.u. isosurface) computed at PBE0/TZP level of the (a) electronic ground state, formally U(VI) f^0 configuration; and (b) electronic state at 3.6 kcal mol^{-1}, formally U(V) f^1 configuration.

Table S1. Occupation number in the localized orbitals for the lowest doublet states of U@C_{27}B, number of electrons over U atom, label of the state and energy in Kcal/mol. Energies of the states are computed at CASPT2 using an imaginary shift of 0.05 Eh and CASSCF energies in parenthesis.

	π_1-cage	π_2-cage	π_3-cage	π_4-cage	$5f_1$-U	$5f_2$-U	π_5-cage	$5f_3$-U	$5f_4$-U	$5f_5$-U	$5f_6$-U	$5f_7$-U	π_6-cage	#el$^-$ in U	Label	E [kcal/mol]
1^2A	1.93	1.95	1.94	0.05	0.00	0.00	0.04	1.00	0.01	0.00	0.01	0.01	0.07	1.03	U(V)-1	7.3 (0.0)
2^2A	1.93	1.94	1.94	0.05	0.00	1.00	0.04	0.00	0.01	0.00	0.01	0.01	0.07	1.03	U(V)-2	12.5 (5.7)
3^2A	1.93	1.94	1.94	0.05	0.99	0.00	0.04	0.00	0.01	0.00	0.01	0.01	0.07	1.03	U(V)-3	13.1 (6.7)
4^2A	1.94	1.94	1.93	0.05	0.00	0.00	0.04	0.00	0.01	0.99	0.01	0.01	0.07	1.03	U(V)-4	14.7 (7.8)
5^2A	1.93	1.94	1.94	0.05	0.00	0.00	0.05	0.00	0.01	0.00	0.01	0.99	0.07	1.02	U(V)-5	13.2 (8.1)
6^2A	1.94	1.93	1.94	0.06	0.00	0.00	0.05	0.00	0.99	0.00	0.01	0.01	0.07	1.02	U(V)-6	14.6 (8.8)
7^2A	1.92	1.94	1.94	0.05	0.00	0.00	0.04	0.00	0.01	0.00	0.99	0.01	0.08	1.02	U(V)-7	12.7 (10.6)
8^2A	1.90	1.87	1.88	0.96	0.01	0.00	0.02	0.00	0.12	0.00	0.05	0.10	0.08	0.29	U(VI)-1	0.0 (25.3)
9^2A	1.88	1.83	1.91	0.02	0.00	0.00	0.95	0.00	0.05	0.00	0.08	0.17	0.10	0.30	U(VI)-2	19.6 (43.7)

$[U@C_{27}B]^+$. We have also calculated the relative energies of the lowest electronic states in the cation species employing the same CASSCF/CASPT2 strategy. In this case, the active space is formed by 6 electrons distributed in the all possible ways over qualitatively the same 13 molecular orbitals (Fig. S5) as for the neutral species. The lowest energy states in this species belong to singlet and triplet multiplicities, the energies and the character of these states appear in the Table S2. These results indicate that the closed-shell singlet is clearly the most stable state in the cationic species.

Table S2. Energy in kcal mol^{-1} and character with the main configuration state functions (CSFs) of the lowest singlet and triplet states of $[U@C_{27}B]^+$. In the character of the CSF, 2 means doubly occupied and u(up) and d(down) refer to singly occupied MO. The label of the orbitals appears in Figure S5. The number of electrons in U are counted in the localized orbitals.

	Energy [Kcal/mol]	Character	#el- in U
1^1A	0.0	$<\varphi_A^2\varphi_B^2\varphi_C^2\|$ (67%)	0.23 U(VI)
2^1A	83.0	$<\varphi_A^2\varphi_B^2\varphi_C^u\varphi_M^d\|$ (30%); $<\varphi_A^u\varphi_B^2\varphi_C^2\varphi_L^d\|$ (20%)	1.01 U(V)
3^1A	86.7	$<\varphi_A^2\varphi_B^2\varphi_C^u\varphi_K^d\|$ (78%)	1.01 U(V)
1^3A	81.7	$<\varphi_A^2\varphi_B^2\varphi_C^u\varphi_H^u\|$ (31%); $<\varphi_A^2\varphi_B^2\varphi_C^u\varphi_K^u\|$ (17%)	1.03 U(V)
2^3A	82.5	$<\varphi_A^2\varphi_B^2\varphi_C^u\varphi_L^u\|$ (43%); $<\varphi_A^2\varphi_B^2\varphi_C^u\varphi_M^u\|$ (24%)	1.03 U(V)
3^3A	85.2	$<\varphi_A^2\varphi_B^2\varphi_C^u\varphi_K^u\|$ (52%)	1.04 U(V)

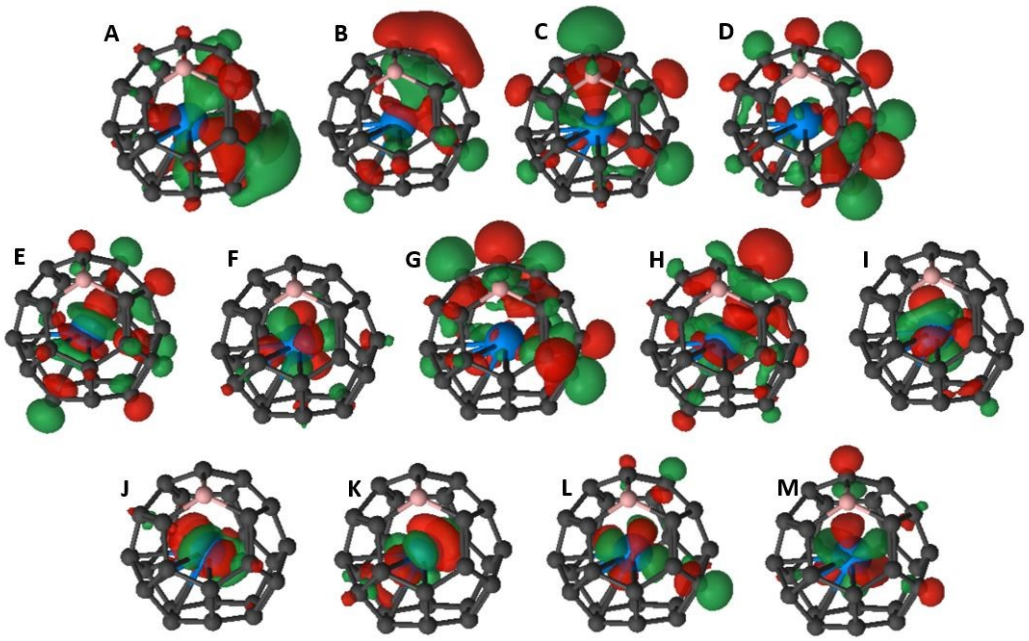


Figure S5. SA(10)-CASSCF natural orbitals for the 10 lowest singlets in $[U@C_{27}B]^+$.

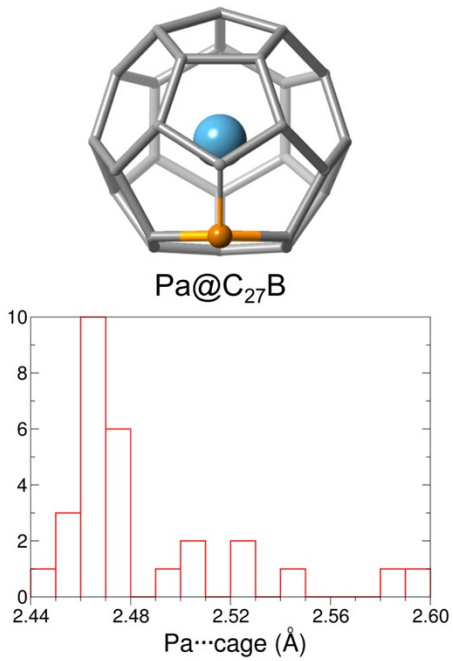


Figure S6. Histogram of the Pa-cage distances in the optimized structure of Pa@C_{27}B. Above, the optimized structure for the isomer 556 is shown.

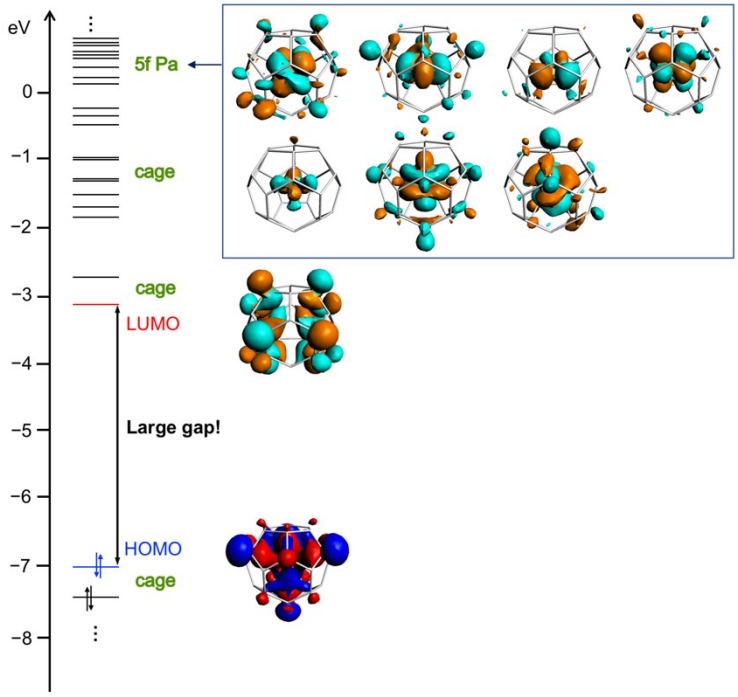


Figure S7. Frontier molecular orbitals of Pa@C_{27}B at PBE0/TZP level. HOMO and LUMO are essentially cage orbitals and all Pa-5f orbitals are empty.

Table S3. Bond critical points (bcp) between the central U and the cage atoms, along with the densities and the Laplacian of the densities at the bcp, for U@C_{27}B.

Atom cage	x	y	z	ρ_{bcp} (e Å^{-3})	$\Delta\rho_{bcp}$ (e Å^{-5})
1	-0.131368	-0.538924	1.367967	0.50	5.36
2	-0.23227	0.306649	1.495469	0.52	4.85
3	0.461971	0.76069	1.356475	0.54	5.32
4	1.055883	0.159679	1.242052	0.54	4.98
5	0.726219	-0.605552	1.223279	0.53	4.94
6	-0.680642	-0.767722	0.813071	0.56	4.96
7	-1.134102	-0.0914	0.571302	0.59	4.79
8	-0.863147	0.544402	0.994445	0.52	5.39
9	-0.536512	1.263678	0.581059	0.53	4.60
10	0.299517	1.314091	0.85942	0.57	4.89
11	0.81741	1.375642	0.115233	0.52	5.32
12	1.359184	0.848443	-0.023747	0.56	4.93
13	1.543515	0.257541	0.520283	0.50	5.34
14	1.477345	-0.496316	0.141454	0.49	4.76
15	0.948431	-1.007839	0.536036	0.51	5.20
16	0.416062	-1.263053	-0.041834	0.53	4.95
17	-0.431149	-1.17321	0.150554	0.50	5.36
18	-0.733273	-0.749493	-0.537228	0.52	4.85
19	-1.165231	-0.096474	-0.23943	0.52	5.40
20	-0.854775	0.589171	-0.713325	0.53	4.62
21	0.244275	1.387249	-0.537864	0.50	4.44
22	0.525748	0.760763	-1.066476	0.53	5.33
23	1.170735	0.454037	-0.786012	0.56	4.92
24	1.252227	-0.359797	-0.666781	0.49	5.34
25	0.560232	-0.887323	-0.770918	0.54	4.98
26	-0.136506	-0.50594	-1.078874	0.54	5.34
27	-0.206813	0.24357	-1.201286	0.57	4.88
28	-0.631707	1.312845	-0.280658	0.45	3.26

Atom 28 is Boron

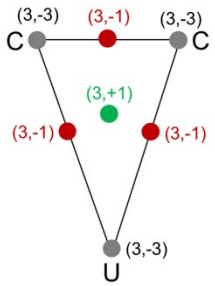


Figure S8. Schematic representation of the atom, bond and ring critical points in a triangle formed by the central U and two bonded C atoms of the cage.

Table S4. Bond critical points (bcp) between the central Pa and the cage atoms, along with the densities and the Laplacian of the densities at the bcp, for $Pa@C_{27}B$. There is no bcp between Pa and boron (atom 21).

Atom cage	x	y	z	ρ_{bcp} (e Å^{-3})	$\Delta\rho_{bcp}$ (e Å^{-5})
1	-0.094442	-0.524307	1.348545	0.50	4.73
2	-0.222773	0.28497	1.475013	0.47	4.65
3	0.469837	0.751319	1.338065	0.51	4.67
4	1.063617	0.16979	1.206421	0.51	4.62
5	0.686114	-0.607355	1.216082	0.50	4.58
6	-0.648618	-0.763279	0.809427	0.52	4.72
7	-1.107693	-0.087201	0.570186	0.54	4.47
8	-0.833966	0.558463	0.973548	0.50	4.66
9	-0.552164	1.207339	0.596407	0.49	4.12
10	0.326741	1.287172	0.844972	0.51	4.50
11	0.78239	1.355201	0.143853	0.50	4.59
12	1.340894	0.826983	-0.002238	0.52	4.58
13	1.501062	0.249834	0.544108	0.49	4.67
14	1.460474	-0.471638	0.138614	0.45	4.57
15	0.926268	-1.000553	0.545153	0.47	4.65
16	0.383319	-1.246268	-0.011215	0.50	4.57
17	-0.389151	-1.150576	0.145153	0.50	4.73
18	-0.709625	-0.742948	-0.503981	0.47	4.65
19	-1.131912	-0.071982	-0.23978	0.50	4.66
20	-0.86121	0.553297	-0.66109	0.49	4.12
22	0.278993	1.353583	-0.520761	0.44	4.18
23	0.489448	0.738281	-1.042813	0.50	4.60
24	1.154502	0.431159	-0.762294	0.52	4.60
25	1.20893	-0.367723	-0.645195	0.49	4.66
26	0.580874	-0.84942	-0.754023	0.51	4.62
27	-0.119127	-0.492731	-1.054974	0.51	4.67
28	-0.169594	0.237503	-1.172875	0.52	4.50

Table S5. Relative energies (in kcal mol^{-1}) of several exohedral U-$C_{27}B$ isomers.

System	Rel. Energy
Exo-1	163.1
Exo-2	160.9
Exo-3	177.5
Exo-4	185.8

In Exo-1, Exo-2 and Exo-3 systems, the U atom is bonded exohedrally to B and C atoms; in Exo-4, the U atom is bonded only to C atoms far from the B atom.

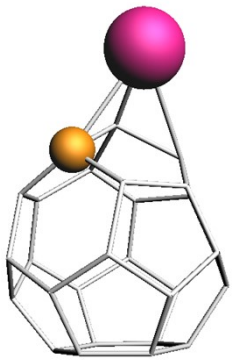


Figure S9. Representation of the optimized structure of exohedral U-$C_{27}B$ system, named Exo-2 in Table S5.

Table S6. QTAIM delocalization indexes for U-cage interactions in U@C_{27}B.

Atom cage	δ (U-cage)
1	0.256
2	0.296
3	0.286
4	0.302
5	0.297
6	0.306
7	0.338
8	0.271
9	0.360
10	0.325
11	0.275
12	0.315
13	0.254
14	0.278
15	0.280
16	0.296
17	0.255
18	0.293
19	0.271
20	0.360
21	0.343
22	0.275
23	0.315
24	0.251
25	0.303
26	0.286
27	0.324
(B) 28	0.097

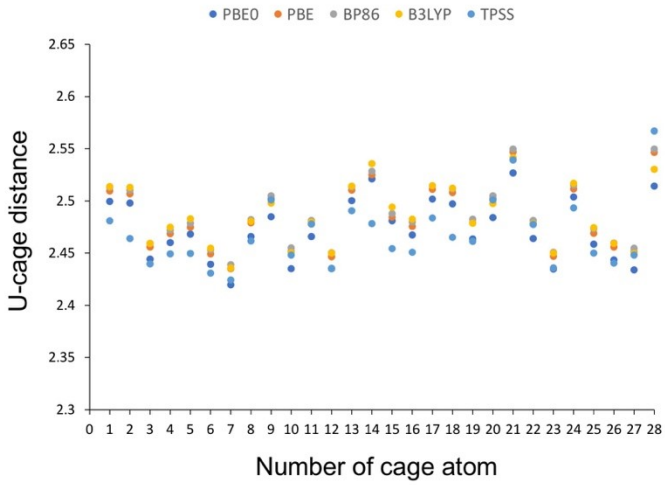


Figure S10. U-cage distances for U@C_{27}B using different density functionals (PBE0, PBE, BP86, B3LYP, TPSS). Cage atom #28 is boron. Very tiny dispersion for the same U-C distance when changing the functional. For U-B distance, the dispersion is somewhat larger, but still within 0.054 Å.

xyz coordinates of optimized structures at PBE0/TZP level

U@$C_{27}B$

C	-0.331620	-1.008171	2.313556
C	-0.553633	0.417211	2.510545
C	0.679227	1.171520	2.287631
C	1.734869	0.194331	2.042345
C	1.113265	-1.156309	2.035328
C	-1.300866	-1.431534	1.310051
C	-2.101599	-0.226603	0.880394
C	-1.603642	0.928661	1.642378
C	-1.069637	2.106253	0.957245
C	0.369369	2.230878	1.334761
C	1.212746	2.354806	0.100778
C	2.248708	1.363250	-0.146012
C	2.569965	0.328092	0.831234
C	2.463390	-0.942609	0.129029
C	1.543422	-1.837312	0.821331
C	0.572612	-2.298881	-0.161578
C	-0.872854	-2.153588	0.116354
C	-1.420029	-1.416862	-1.014188
C	-2.150761	-0.232074	-0.589397
C	-1.640015	0.899345	-1.362978
C	0.322894	2.341119	-1.051477
C	0.703304	1.276599	-1.969105
C	1.927073	0.682698	-1.454343
C	2.059404	-0.758625	-1.257780
C	0.875722	-1.622065	-1.450171
C	-0.361866	-1.032617	-1.947464
C	-0.495118	0.401349	-2.181645
B	-1.139118	2.134087	-0.583894
U	0.176214	0.117585	0.140393

U@$C_{27}B^{+}$

C	0.853660	-1.939908	-1.256393
C	-0.242170	-1.404839	-2.046407
C	0.050944	-0.033726	-2.453266
C	1.413412	0.254057	-2.016692
C	1.919864	-0.943832	-1.264125
C	0.284565	-2.421606	0.000000
C	-1.185199	-2.090662	0.000000
C	-1.484207	-1.426481	-1.280840
C	-2.069277	-0.103278	-1.332641
C	-1.073019	0.789831	-2.026269
C	-0.810319	1.975863	-1.183920
C	0.553399	2.275201	-0.752504
C	1.656234	1.427855	-1.190828
C	2.365643	0.977964	0.000000
C	2.473013	-0.474266	0.000000
C	1.919864	-0.943832	1.264125
C	0.853660	-1.939908	1.256393
C	-0.242170	-1.404839	2.046407
C	-1.484207	-1.426481	1.280840
C	-2.069277	-0.103278	1.332641
C	-1.652744	1.909803	0.000000
C	-0.810319	1.975863	1.183920
C	0.553399	2.275201	0.752504
C	1.656234	1.427855	1.190828
C	1.413412	0.254057	2.016692
C	0.050944	-0.033726	2.453266
C	-1.073019	0.789831	2.026269
B	-2.444048	0.578932	0.000000
U	0.033724	0.006349	0.000000

U-C_{27}B exohedral (Exo-2)

C	-0.298979	-1.068231	2.264919
C	-0.546497	0.352377	2.520953
C	0.666372	1.111016	2.323252
C	1.690665	0.181471	2.012222
C	1.090093	-1.203706	1.986173
C	-1.250209	-1.486427	1.298882
C	-2.067212	-0.259662	0.903910
C	-1.583958	0.855311	1.663453
C	-1.077663	2.053339	0.997491
C	0.336374	2.129525	1.342326
C	1.189723	2.335540	0.198996
C	2.163521	1.346403	-0.088454
C	2.502800	0.327136	0.847095
C	2.441356	-0.932149	0.121357
C	1.534935	-1.850047	0.790106
C	0.579786	-2.281039	-0.172259
C	-0.811370	-2.129601	0.106488
C	-1.384862	-1.386521	-1.004024
C	-2.109425	-0.228823	-0.532067
C	-1.622444	0.903655	-1.257322
C	0.335632	2.570878	-1.111957
C	0.633058	1.276500	-1.845257
C	1.847702	0.705750	-1.395835
C	2.000931	-0.709515	-1.243091
C	0.872289	-1.554078	-1.458791
C	-0.343617	-0.988974	-1.933403
C	-0.472117	0.433757	-2.074185
B	-1.197882	2.150370	-0.525039
U	-0.086000	4.408745	-0.431939

Pa@C_{27}B

C	-0.316464	-0.987268	2.303089
C	-0.549361	0.432763	2.543238
C	0.686348	1.188581	2.305619
C	1.751498	0.203346	2.056254
C	1.119598	-1.165764	2.051579
C	-1.320276	-1.440384	1.325850
C	-2.126598	-0.237582	0.898671
C	-1.594291	0.932543	1.643195
C	-1.084540	2.119314	0.958996
C	0.377463	2.250597	1.345074
C	1.197367	2.352633	0.102787
C	2.269716	1.374840	-0.150967
C	2.547941	0.322035	0.833886
C	2.488148	-0.966933	0.142872
C	1.559315	-1.857718	0.834891
C	0.576649	-2.313827	-0.155236
C	-0.856212	-2.127994	0.109675
C	-1.429649	-1.428110	-1.035054
C	-2.142595	-0.227207	-0.587366
C	-1.654587	0.913730	-1.359315
B	-1.166134	2.193809	-0.602471
C	0.316226	2.381044	-1.064503
C	0.691396	1.282493	-1.954609
C	1.948136	0.694700	-1.459209
C	2.039056	-0.753518	-1.233918
C	0.886256	-1.626514	-1.460925
C	-0.363494	-1.031896	-1.962758
C	-0.493228	0.408655	-2.195865
Pa	0.179614	0.108913	0.151009