Supplementary Material

Stabilizing Antiaromatic C_{13} through Metal Encapsulation: A Dual Stabilization Mechanism Achieving Closed-Shell Noble-Gas-Like Metal Centers and Double Aromaticity

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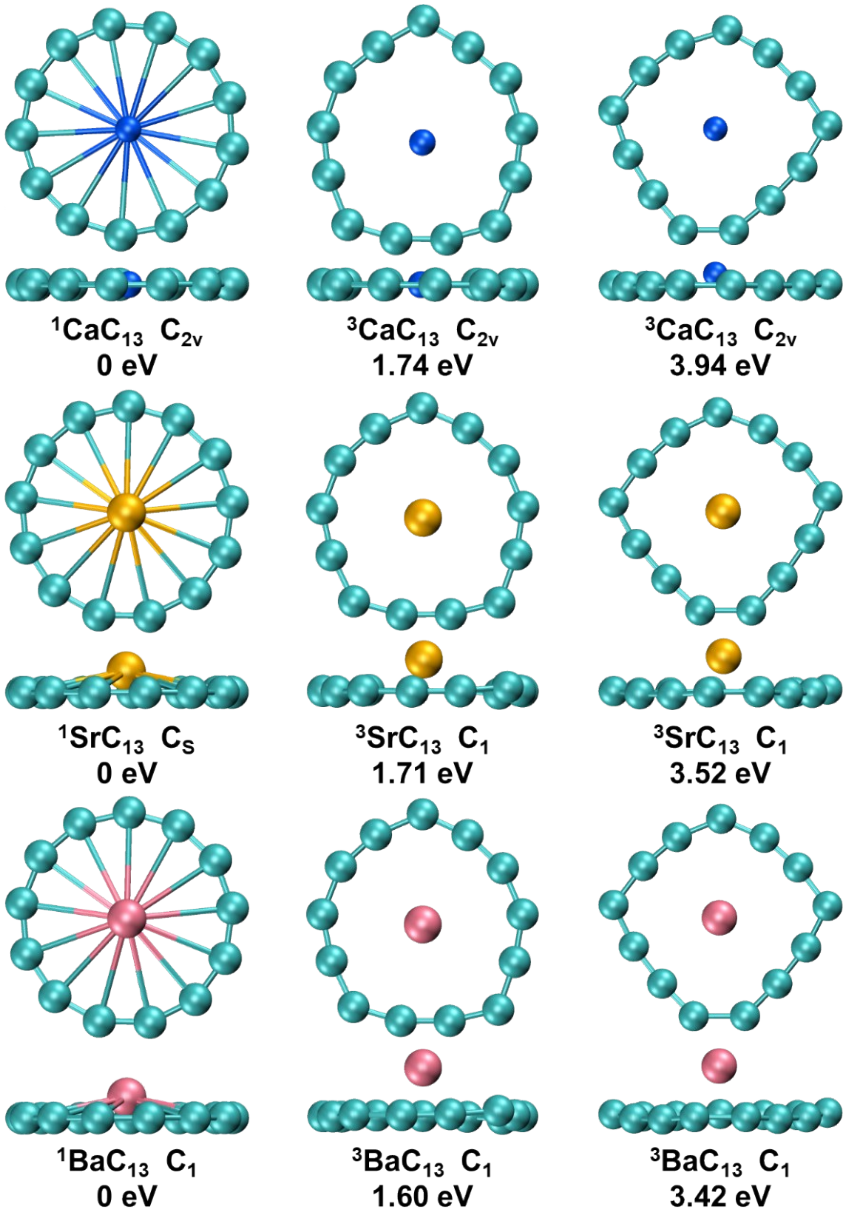

Fig. S1. Top and side views of geometric configurations for endohedral MC_{13} (where M represents Ca, Sr, or Ba) featuring different spin multiplicities calculated at the ωB97X-D/def2-TZVP level, respectively. The energy value denotes the energy difference between triplet/quintet-state and singlet-state structures.

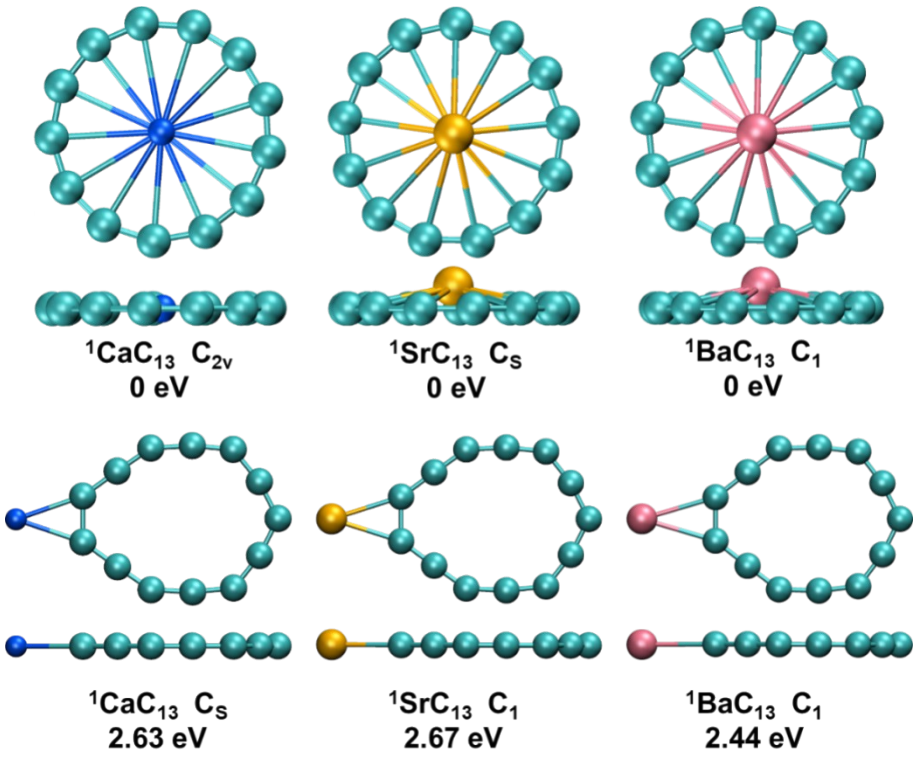

Fig. S2. Singlet-state geometric configurations of endohedral MC_{13} and exohedral MC_{13} (M = Ca, Sr, and Ba) calculated at the ωB97X-D/def2-TZVP level, respectively. The energy value corresponds to the energy difference between exohedral isomers (metal atom outside the ring) and the most stable endohedral structures (metal atom inside the ring).

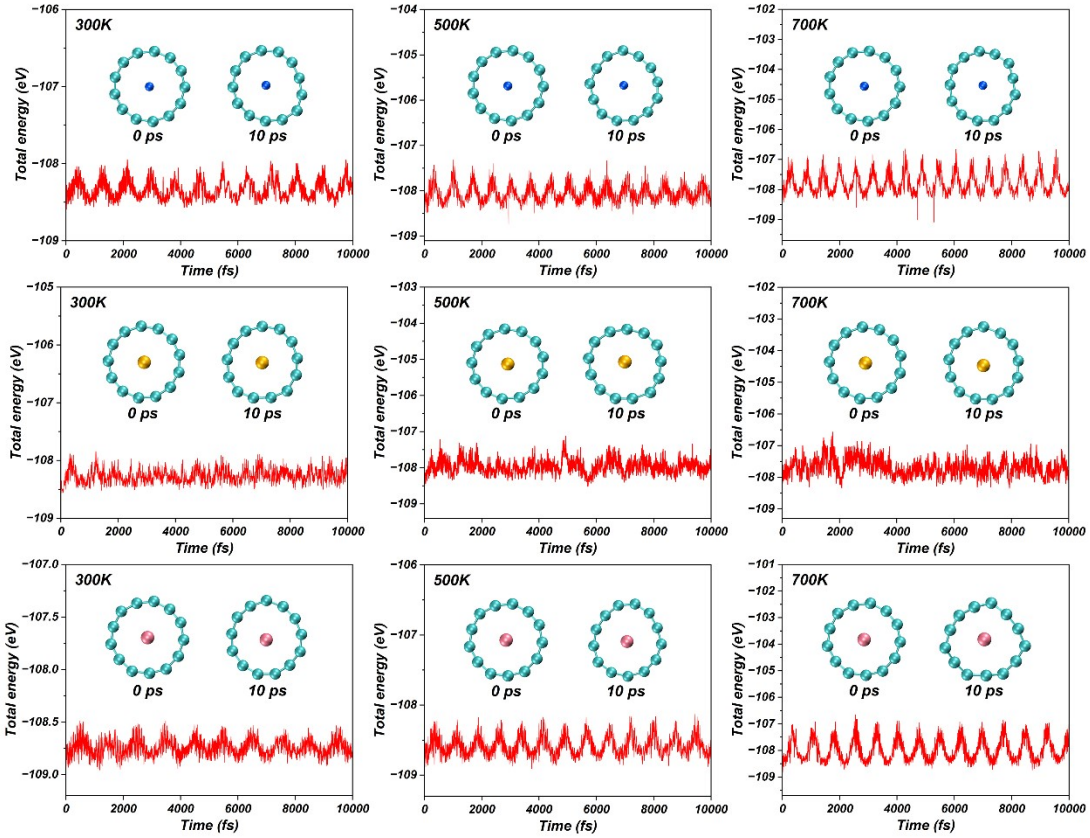

Fig. S3. AIMD simulations of (a) CaC_{13}, (b) SrC_{13}, and (c) BaC_{13} at 300 K, 500 K, and 700 K over 10 ps, respectively.

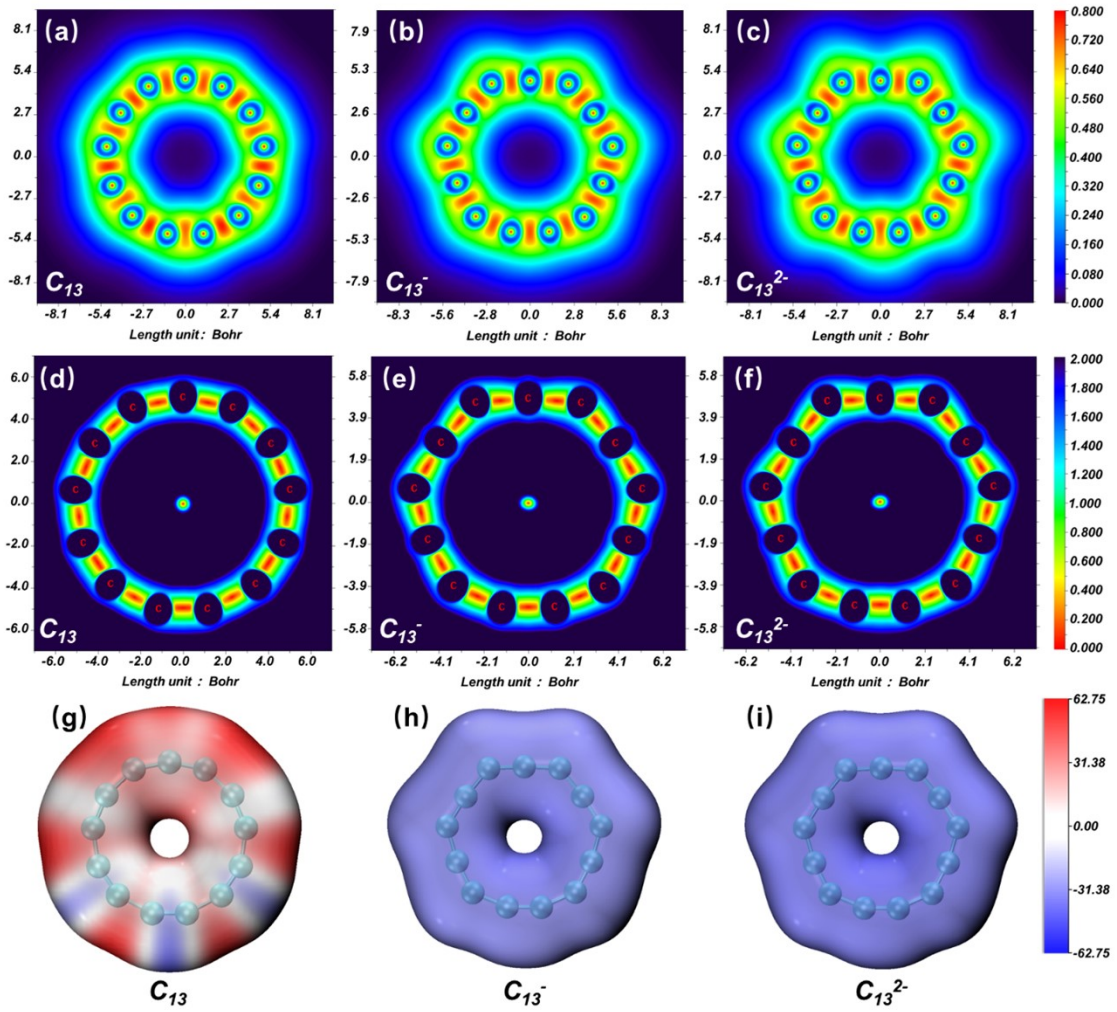

Fig. S4. Color-filled two-dimensional maps of the (a-c) localized orbital locator (LOL), (d-f) interaction region indicator (IRI), and (g-i) electrostatic potential (ESP) of C_{13}, C_{13}^-, and C_{13}^{2-}.

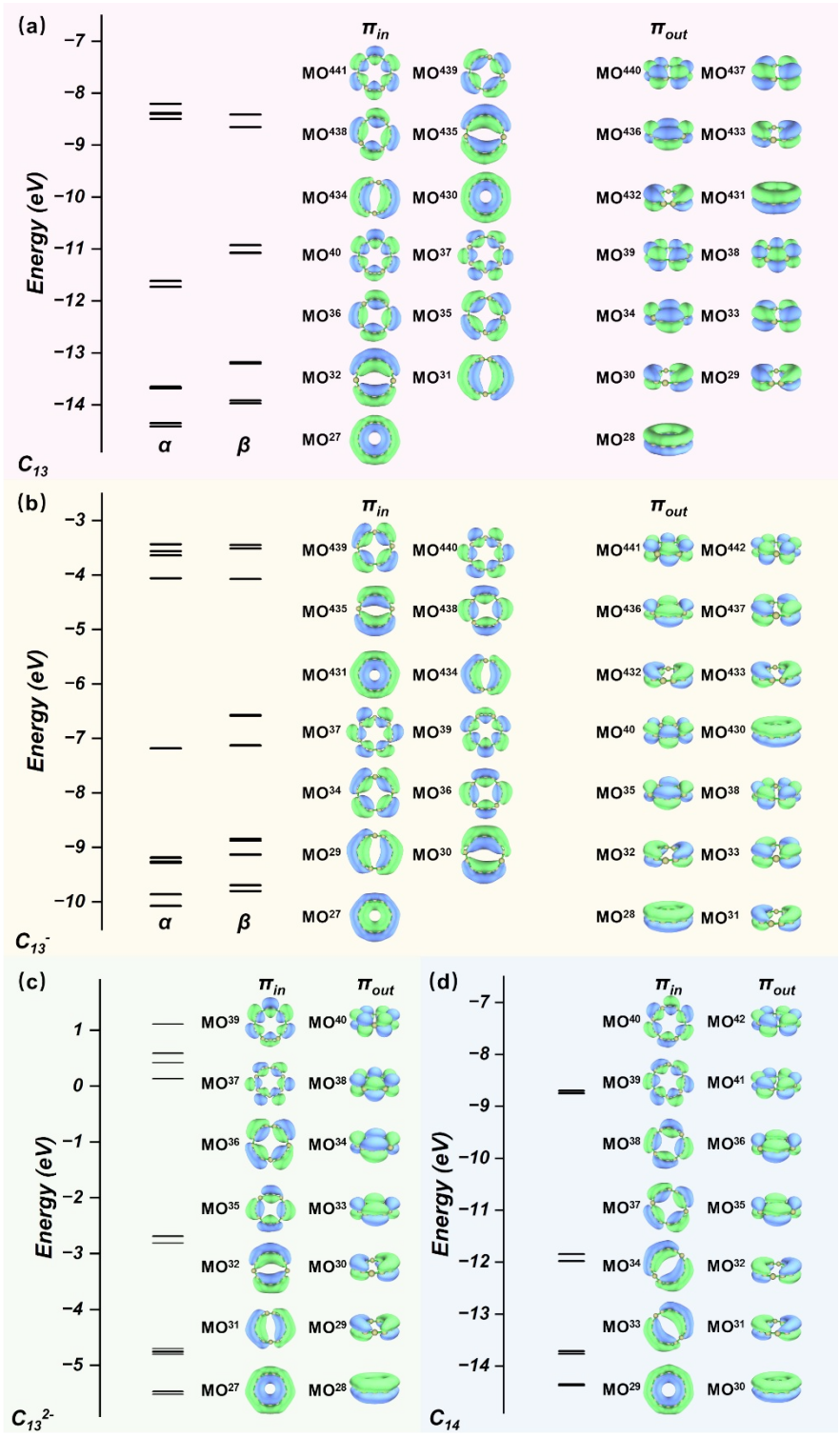

Fig. S5. The orbital energy diagrams and spatial distributions of canonical molecular orbitals (CMOs, isovalue = 0.02 a.u.) of (a) C_{13}, (b) C_{13}^-, (c) C_{13}^{2-} and (d) C_{14}. The spatial distributions of the occupied in-plane and out-of-plane π orbitals are depicted separately to the right of the orbital energy diagrams.

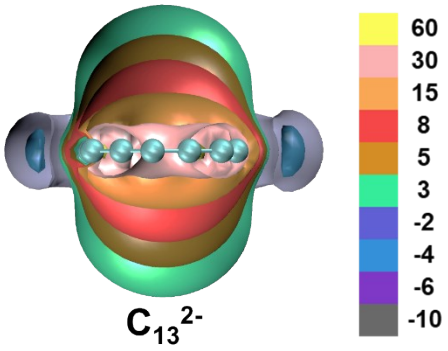

Fig. S6. Multiple clipped isosurfaces of $ICSS_{zz}$ of the C_{13}^{2-} dianion.

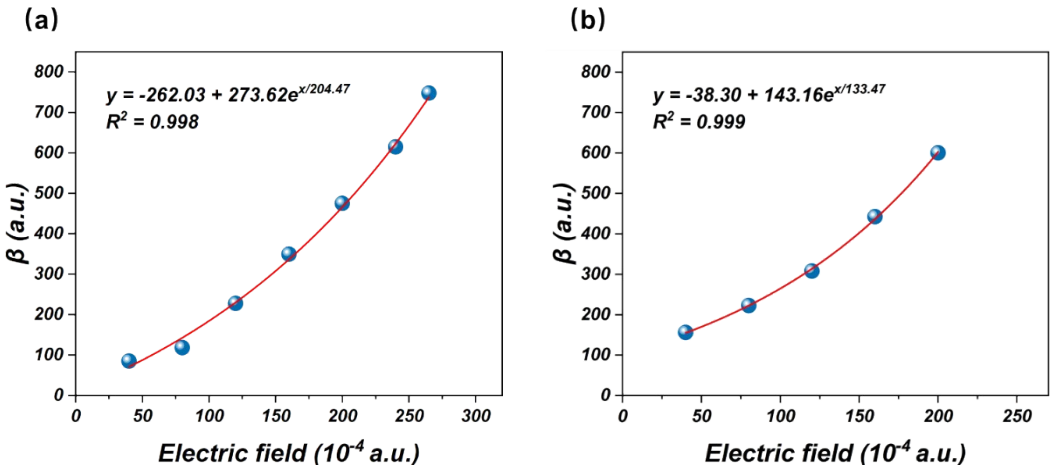

Fig. S7. Variation curve of β_0 for (a) SrC_{13} and (b) BaC_{13} with OEEF.

Table S1. Energies (in eV) of triplet-state endohedral MC_{13}, singlet-state endohedral MC_{13}, and singlet-state exohedral MC_{13} (M = Ca, Sr, Ba) calculated at the ωB97X-D/def2-TZVP level with SDD basis sets added for Ca, Sr, and Ba atoms, respectively. The endohedral singlet configuration is the most stable, and Δ*E* (in eV) denotes the energy difference relative to this minimum-energy structure for triplet endohedral and singlet exohedral configurations.

System	M-site	Multiplicities	Electronic Energy (eV)	Δ*E* (eV)
CaC_{13}	Inside	Singlet	-14469.20	0.00
		Triplet	-14467.46	1.74
		Quintet	-14465.71	3.49
	Outside	Singlet	-14466.56	2.63
SrC_{13}	Inside	Singlet	-14303.27	0.00
		Triplet	-14301.57	1.71
		Quintet	-14299.76	3.52
	Outside	Singlet	-14300.61	2.67
BaC_{13}	Inside	Singlet	-14161.30	0.00
		Triplet	-14159.70	1.60
		Quintet	-14157.88	3.42
	Outside	Singlet	-14158.86	2.44

Table S2. Cartesian coordinates of optimized C_{13} and MC_{13} (M = Ca, Sr, and Ba).

C_{13} (Charge = 0; Spin multiplicity = 3)

C	2.20417200	1.50314400	0.00000000
C	2.67705100	0.35566300	0.00000000
C	2.49516200	-0.97656000	0.00000000
C	1.81699600	-1.99573400	0.00000000
C	0.61145100	-2.61954400	0.00000000
C	-0.60819800	-2.62207500	0.00000000
C	-1.81086000	-1.99679700	0.00000000
C	-2.49235000	-0.97593700	0.00000000
C	-2.68039200	0.34936700	0.00000000
C	-2.20235200	1.50274600	0.00000000
C	-1.25590500	2.40561000	0.00000000
C	0.00000000	2.66282600	0.00000000
C	1.24522600	2.40729000	0.00000000

CaC_{13} (Charge = 0; Spin multiplicity = 1)

C	-1.65000000	2.12500000	0.00000000
C	-0.47400000	2.64400000	0.00000000
C	-0.17700000	-2.67800000	0.00000000
C	0.80900000	2.56300000	0.00000000
C	1.90600000	1.89200000	0.00000000
C	2.63900000	-0.49500000	0.00000000
C	2.56700000	0.78900000	0.00000000
C	2.10600000	-1.66500000	0.00000000
C	1.08900000	-2.45300000	0.00000000
C	-1.40400000	-2.29100000	0.00000000
C	-2.44600000	1.11500000	0.00000000
C	-2.30700000	-1.37700000	0.00000000
C	-2.68600000	-0.14800000	0.00000000
Ca	0.00900000	-0.00700000	0.00000000

SrC_{13} (Charge = 0; Spin multiplicity = 1)

C	-2.54000000	-0.89900000	-0.17900000
C	-2.66700000	0.38300000	-0.17900000
C	2.49800000	-1.01000000	-0.17900000
C	-2.18300000	1.57900000	-0.17900000
C	-1.19900000	2.41200000	-0.17900000
C	1.30400000	2.35600000	-0.17900000
C	0.05900000	2.69400000	-0.17800000

C	2.25100000	1.48200000	-0.17800000
C	2.68100000	0.26600000	-0.17900000
C	1.74200000	-2.05400000	-0.18000000
C	-1.83100000	-1.97700000	-0.17800000
C	0.58800000	-2.63000000	-0.17900000
C	-0.70200000	-2.60000000	-0.17900000
Sr	0.00000000	0.00000000	0.36700000

BaC_{13} (Charge = 0; Spin multiplicity = 1)

C	1.15300000	2.47200000	-0.46600000
C	2.10000000	1.61500000	-0.49400000
C	-2.47600000	-1.10100000	-0.47500000
C	2.70000000	0.46500000	-0.46000000
C	2.51700000	-0.80900000	-0.49500000
C	0.76500000	-2.53400000	-0.49300000
C	1.92400000	-1.95200000	-0.46000000
C	-0.50500000	-2.68200000	-0.46500000
C	-1.66200000	-2.07800000	-0.49100000
C	-2.67600000	0.19400000	-0.48600000
C	-0.14000000	2.65900000	-0.49000000
C	-2.28900000	1.40200000	-0.48400000
C	-1.36900000	2.33600000	-0.47500000
Ba	-0.00400000	0.00100000	0.66800000

Table S3. The results of sobEDAw calculation for MC_{13} (M = Ca, Sr, Ba), divided into neutral fragments: M and the C_{13} (triplet), charged fragments: the metal cation M^+ and the C_{13}^- (singlet) and charged fragments: the metal cation M^{2+} and the C_{13}^{2-} (singlet).

Term	**Energy (kcal/mol)**		
	^{1}**Ca + ^{3}C$_{13}$**	^{1}**Ca$^+$ + ^{1}C$_{13}^-$**	^{1}**Ca^{2+} + ^{1}C$_{13}^{2-}$**
ΔE_{int}	-46.62	-92.85	-485.02
ΔE_{els}[a]	-215.84 (49.45%)	-205.41 (62.43%)	-408.45 (75.37%)
ΔE_{orb}[a]	-184.01 (42.15%)	-90.83 (27.60%)	-113.62 (20.97%)
ΔE_{disp}[a]	-36.65 (8.40%)	-32.81(9.97%)	-19.83 (3.66%)
ΔE_{xrep}	389.88	236.2	56.88
Term	**Energy (kcal/mol)**		
	^{1}**Sr + ^{3}C$_{13}$**	^{1}**Sr$^+$ + ^{1}C$_{13}^-$**	^{1}**Sr^{2+} + ^{1}C$_{13}^{2-}$**
ΔE_{int}	-42.88	-92.85	-449.62
ΔE_{els}[a]	-226.12 (49.46)	-205.41 (62.43%)	-406.17 (76.42%)
ΔE_{orb}[a]	-192.36 (42.08%)	-90.83 (27.60%)	-102.53 (19.29%)
ΔE_{disp}[a]	-38.69 (8.46%)	-32.81 (9.97%)	-22.78 (4.29%)
ΔE_{xrep}	414.29	236.2	81.84
Term	**Energy (kcal/mol)**		
	^{1}**Ba + ^{3}C$_{13}$**	^{1}**Ba$^+$ + ^{1}C$_{13}^-$**	^{1}**Ba^{2+} + ^{1}C$_{13}^{2-}$**
ΔE_{int}	-60.00	-96.57	-424.54
ΔE_{els}[a]	-204.19 (46.33%)	-192.26 (59.53%)	-385.95 (75.23%)
ΔE_{orb}[a]	-198.14 (44.96%)	-97.62 (30.23%)	-102.84 (20.05%)
ΔE_{disp}[a]	-38.36 (8.70%)	-33.09 (10.25%)	-24.22 (4.72%)
ΔE_{xrep}	380.69	226.4	88.47