Supplementary Material (ESI) for *PCCP*

Mercury dications: linear form is more stable than aromatic ring

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Summpelemtary Material

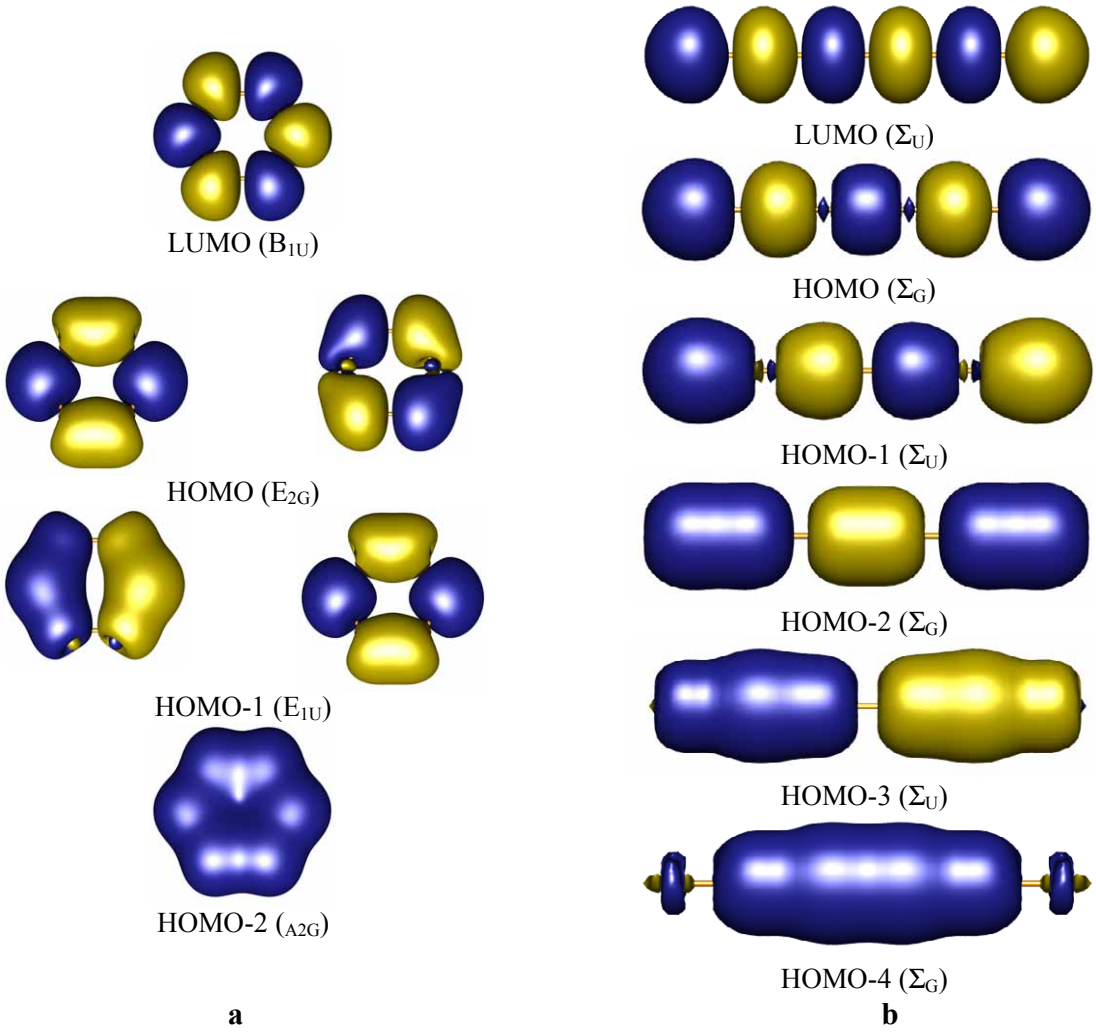

Figure 1S Molecular orbitals (BP86/cc-pVTZ-PP) of the **a**) cyclic and **b**) linear isomer of Hg_6^{2+}.

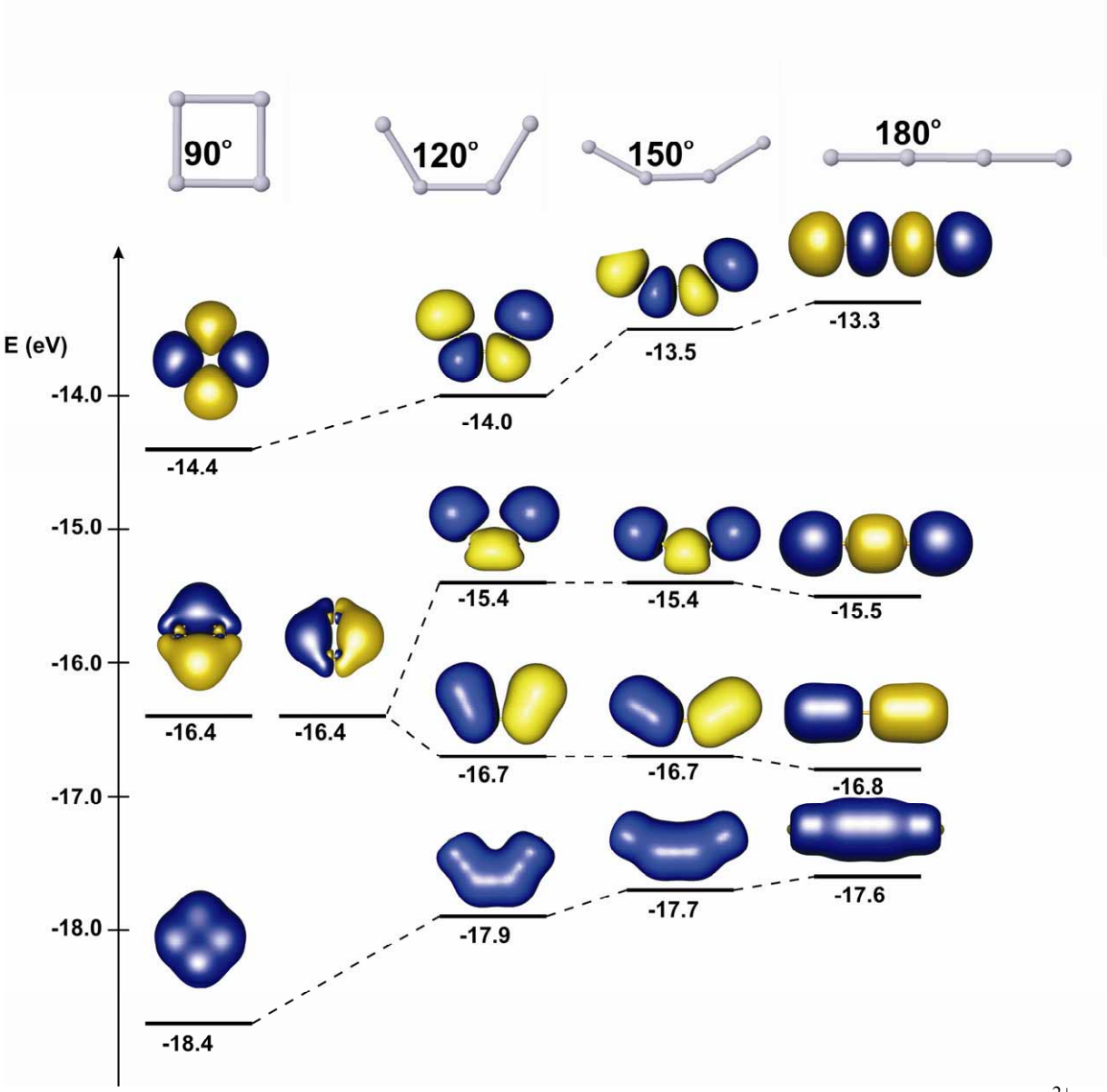

Figure 2S Orbital correlation diagram for the D_{4h}, linear and intermediate geometries of Hg_4^{2+}.

Table 1S Geometric parameters and relative energies of Hg_4^{2+} isomers using different methods. The cc-pVTZ-PP basis set was applied in all cases.

Method	BP86		QCISD		QCISD(T)	
Isomer	linear	D_{4h}	linear	D_{4h}	linear	D_{4h}
Bond	Bond lengths in Å					
1	2.736	2.924	2.700	2.880	2.696	2.874
2	2.692	2.924	2.636	2.880	2.639	2.874
3	2.736	2.924	2.700	2.880	2.696	2.874
4	-	2.924	-	2.880	-	2.874
E_{rel} (kJ/mol)	0	112	0	124	0	111
NICS (ppm)	-	-14.1	-	-	-	-
$NICS_{zz}$ (ppm)	-	-10.7	-	-	-	-

Table 2S Geometric parameters and relative energies of Hg_6^{2+} isomers using different methods. The cc-pVTZ-PP basis set was applied in all cases.

Method	BP86		QCISD	
Isomer	linear	D_{6h}	linear	D_{6h}
Bond	Bond lengths in Å			
1	2.820	2.876	2.811	2.834
2	2.744	2.876	2.688	2.834
3	2.726	2.876	2.658	2.834
4	2.744	2.876	2.688	2.834
5	2.820	2.876	2.811	2.834
6	-	2.876	-	2.834
Erel (kJ/mol)	0	107	0	119
NICS (ppm)	-	-16.4	-	-
$NICS_{zz}$ (ppm)	-	-34.3	-	-

Table 3S Relative energies of the ring isomers compared to the linear clusters using CCSD(T) method and different basis sets on QCISD(T)/cc-pVTZ-PP geometries for the Hg_4^{2+} clusters and QCISD/cc-pVTZ-PP geometries for Hg_6^{2+} clusters.

	Hg_4^{2+}	Hg_6^{2+}
aug-cc-pVDZ-PP	110.3	102.4
aug-cc-pVTZ-PP	111.4	102.0
aug-cc-pVQZ-PP	110.9	-
CBS(DTQ)	111.2	-

Complete basis set (CBS) value was extrapolated using the aug-cc-pVXZ-PP (X=D, T, Q) basis sets and the default extrapolation procedure of Molpro.

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