Why do the Heavy-Atom Analogues of Acetylene E_2H_2 ($E = Si - Pb$) Exhibit Unusual Structures?

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Supporting Information (4 Tables and complete references 24 and 29)

Table S1. Energy Decomposition Analysis of E₂H₂ Isomer **D2** (E = Si, Ge, Sn, Pb) Using EH as Fragments. The Energy Values are Given in kcal/mol. The E₂H₂ Structures were Optimized with the E-E Distance Frozen at the Value in **A**.

Term	Si ₂ H ₂	Ge ₂ H ₂	Sn ₂ H ₂	Pb ₂ H ₂
ΔE_{int}	-30.23	-29.79	-28.66	-27.69
ΔE_{Pauli}	226.17	203.52	165.59	146.20
$\Delta E_{\text{elstat}}^{\text{a}}$	-139.57 (54.4%)	-138.44 (59.3%)	-122.71 (63.2%)	-113.52 (65.3%)
$\Delta E_{\text{orb}}^{\text{a}}$	-116.83 (45.6%)	-94.86 (40.7%)	-71.55 (36.8%)	-60.37 (34.7%)
$\Delta E(\text{A}')^{\text{b}}$	-116.77 (99.9%)	-94.46 (99.6%)	-71.09 (99.4%)	-59.85 (99.1%)
$\Delta E(\text{A}'')^{\text{b}}$	-0.06	-0.40	-0.46	-0.53

^a The value in parentheses gives the percentage contribution to the total attractive interactions ΔE_{elstat} + ΔE_{orb} .

^b The value in parentheses gives the percentage contribution to the total orbital interactions ΔE_{orb} .

Table S2. Energy Decomposition Analysis of E₂H₂ Isomer **D1** (E = Si, Ge, Sn, Pb) Using EH as Fragments. The Energy Values are Given in kcal/mol. Single-point Calculations of E₂H₂ with the E-E, E-H Distances and the E-E-H Angle were Taken from **B** Isomer.

Term	Si ₂ H ₂	Ge ₂ H ₂	Sn ₂ H ₂	Pb ₂ H ₂
ΔE_{int}	-48.73	-33.55	-26.12	-19.72
ΔE_{Pauli}	258.42	231.91	170.52	116.75
$\Delta E_{\text{elstat}}^{\text{a}}$	-123.42 (40.2%)	-126.78 (47.8%)	-101.60 (51.7%)	-73.33 (53.7%)
$\Delta E_{\text{orb}}^{\text{a}}$	-183.71 (59.8%)	-138.69 (52.2%)	-95.04 (48.3%)	-63.15 (46.3%)
$\Delta E(\text{A}')^{\text{b}}$	-143.43 (78.1%)	-103.54 (74.7%)	-68.12 (71.7%)	-40.38 (63.9%)
$\Delta E(\text{A}'')^{\text{b}}$	-40.28 (21.9%)	-35.15 (25.3%)	-26.92 (28.3%)	-22.77 (36.1%)

^a The value in parentheses gives the percentage contribution to the total attractive interactions ΔE_{elstat} + ΔE_{orb} .

^b The value in parentheses gives the percentage contribution to the total orbital interactions ΔE_{orb} .

Table S3. Calculated Absolute Energies (in Hartrees) and Relative Energies (in kcal/mol) of the Si₂H₂ Isomers **A - I(T)** at the MRCI-SD/aug-cc-pVQZ and MRCI-SD(Q)/aug-cc-pVQZ Levels of Theory. The Values for a0 Give the Coefficients of the Hartree-Fock Reference Configuration in the MRCI Expansion.

Isomer	MRCI-SD	E _{rel}	a0	MRCI-SD(Q)	E _{rel}
A	-579.225739	0.00	0.910167	-579.244124	0.00
B	-579.210484	9.57	0.898714	-579.227837	10.22
D2	-579.161488	40.32	0.899292	-579.178200	41.37
D1	-579.199778	16.29	0.871612	-579.215681	17.85
F	-579.158034	42.49	0.898322	-579.173953	44.03
G	-579.208463	10.84	0.896531	-579.226580	11.01
E	-579.166180	37.37	0.893831	-579.182032	38.96
C	-579.207041	11.73	0.900137	-579.223486	12.95
A(T)	-579.141195	53.05	0.909555	-579.165940	49.06
B(T)	-579.172950	33.13	0.915816	-579.189931	34.01
D(T)	-579.185465	25.27	0.903987	-579.202590	26.06
F(T)	-579.165545	37.77	0.891867	-579.183031	38.34
H(T)	-579.170284	34.80	0.898845	-579.187276	35.67
G(T)	-579.138789	54.56	0.910920	-579.164224	50.14
E(T)	-579.088377	86.20	0.856040	-579.107189	85.93
C(T)	-579.191069	21.76	0.921046	-579.208256	22.51
I(T)	-579.170582	34.61	0.912800	-579.188531	34.89

Table S4. Calculated Energies of the E₂H₂ Forms **A - E** (in Hartrees) of ADF at BP86/QZ4P. The Program Gives Only Relative Energies of the Molecules with Respect to the Energies of the Atoms.

E	A	B	C	D1	D2	E
C	-	-	-	-	-	-0.83566647
Si	-0.50783625	-0.49212019	-0.48340284	-0.47605401	-0.43508475	-0.44176921
Ge	-0.46747420	-0.45006212	-0.44119501	-0.43192511	-0.40758219	-0.37865701
Sn	-0.42119093	-0.39960403	-0.39047666	-0.38089957	-0.37449437	-0.31822014
Pb	-0.39995839	-0.37283746	-0.35683265	-0.35058272	-0.35777119	-0.25254951

Complete References

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