Ab Initio Study of Lead Hydride Cation: $Pb_2H_2^+$

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Introduction

- Lead is known for its toxicity[1], but it is prevalent in multiple industries for its unique electronic and chemical properties.
- In 2022, 92% of lead consumption was lead-acid batteries according to the USGS.[2]
- Investigating the unique properties of Lead Hydride Cation and the trends of group 14 hydrides.

Methodology

- Geometries and harmonic frequency calculations were completed at CCSD(T)/cc-pwCVQZ-PP level of theory.
- Anharmonic frequency calculation were completed at CCSD(T)/cc-pwCVTZ-PP level of theory
- Natural Bond Order analysis was completed to determine the dipole moment and bonding order for Pb-Pb and Pb-H bonds.
- Focal Point Analysis and Relative energy corrections will be completed for each isomer.

Relative Energies

Lead Hydride Isomer	Relative Energies(kcal/mol)
butterfly	0.0
cis	29.97
linear	97.40
trans	28.84
monobridged	19.26
Vinylidene-like	26.57
planar	1.05

Table 1: Relative energies in kcal/mol of the seven lead hydride isomers at CCSD(T)/cc-pwCVQZ-PP level of theory.

Optimized Geometries

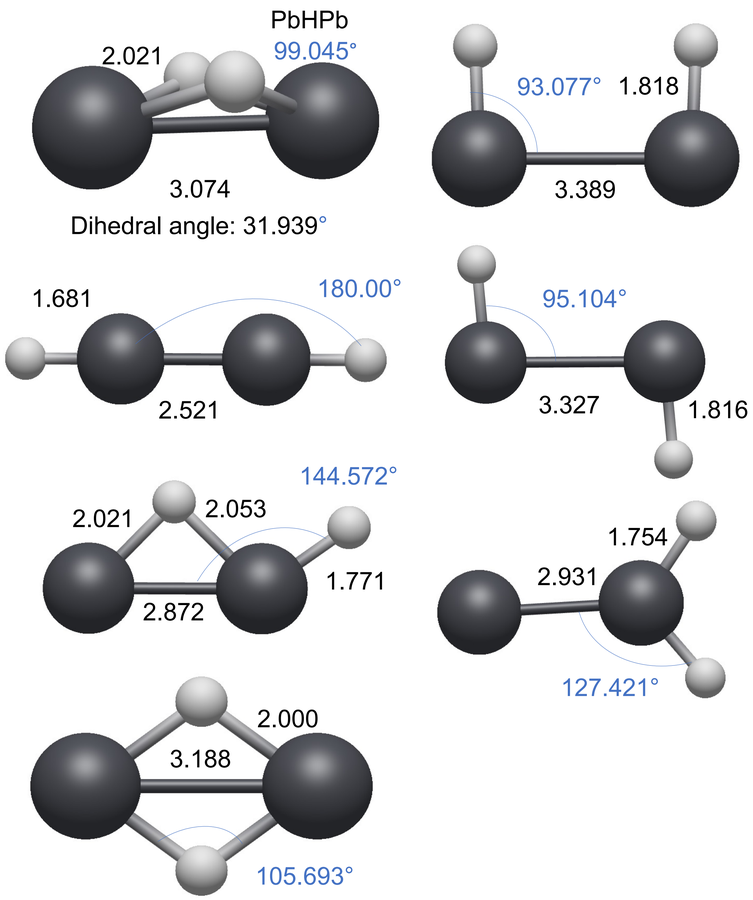

Figure 1: Optimized geometries for the seven isomers of Lead Hydride at CCSD(T)/cc-pwCVQZ-PP level of theory. All bond distances are in Angstrom and angles in degrees.
1st row(L to R): butterfly, cis
2nd row(L to R): linear, trans
3rd row(L to R): monobridged, vinylidene-like
4th row: planar

Bond Orders

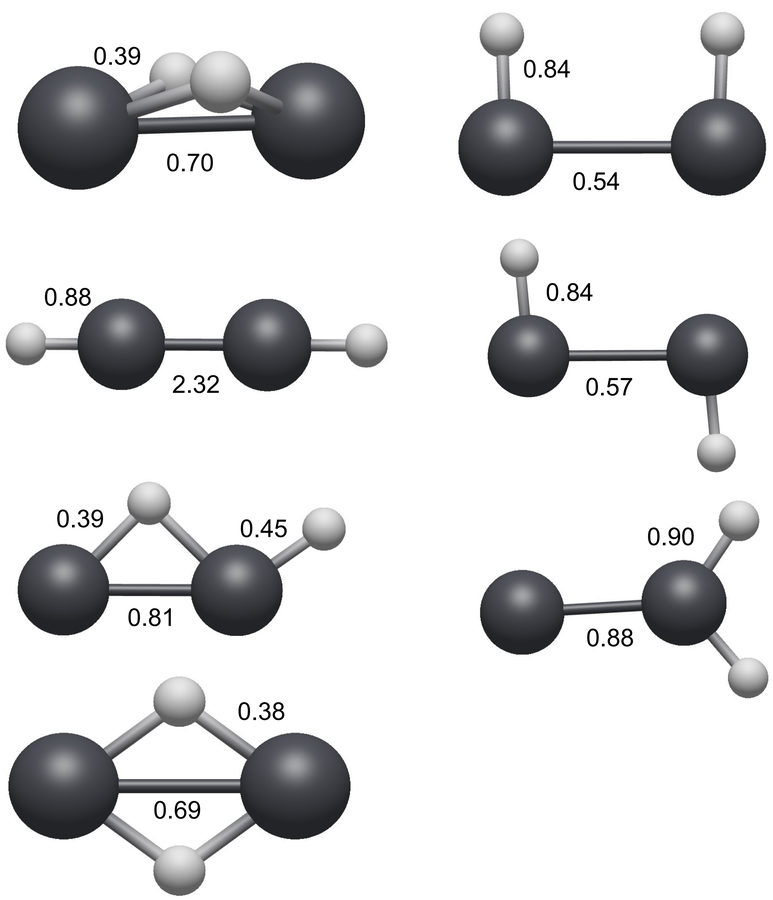

Figure 2: Wiberg Bond Order of each Pb-Pb and Pb-H.
1st row(L to R): butterfly, cis
2nd row(L to R): linear, trans
3rd row(L to R): monobridged, vinylidene-like
4th row: planar

Acknowledgement and References

We acknowledge support from the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES) under Contract No. DE-SC0018412.

1. Wani AL, Ara A, Usmani JA. *Interdiscip Toxicol*. 2015;8(2):55-64.
2. U.S. Geological Study. Lead. 2022 Mineral Commodity Summary.

Conclusions

- The butterfly isomer was found to lie lowest in energy according to the cc-pwCVQZ-PP basis set
- The butterfly, vinylidene-like, and monobridged isomers are local minima, while the other four isomers are transition states.

A Computational Study of the Lead Hydride Cation: $Pb_2H_2^+$

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- Anharmonic frequency calculations were completed at CCSD(T)/cc-pwCVTZ-PP level of theory.
- Natural Bond Order analysis was completed to determine the dipole moment and bonding order for Pb-Pb and Pb-H bonds.
- Focal Point Analysis and energy corrections will be completed for each isomer.

Geometries

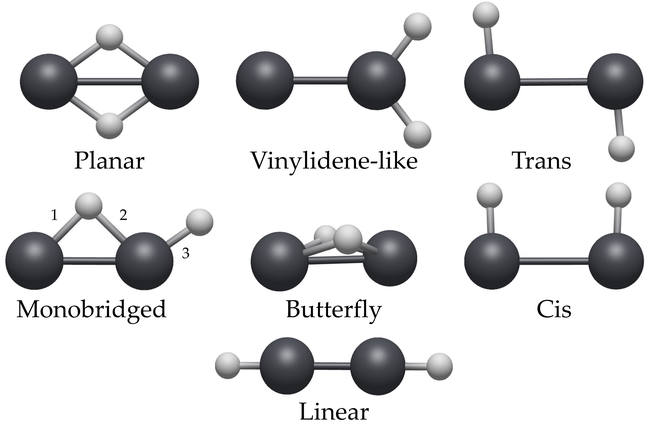

Figure 1: CCSD(T)/cc-pwCVQZ-PP optimized geometries of the seven $Pb_2H_2^+$ isomers. Select Pb–H bonds are labeled.

Relative Energies

Isomer	Relative Energies (kcal mol^{-1})
Butterfly	0.00
Planar	1.05
Monobridged	19.26
Vinylidene-like	26.57
Trans	28.84
Cis	29.97
Linear	97.40

Table 1: Relative energies in kcal mol^{-1} of the seven $Pb_2H_2^+$ isomers at CCSD(T)/cc-pwCVQZ-PP level of theory.

Focal Point Analysis

Basis Set	HF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aVDZ	-23.32	+4.64	-4.01	+0.30	-0.10	-0.05	[-22.54]
aVTZ	-23.54	+4.52	-4.20	+0.27	[-0.10]	[-0.05]	[-23.09]
aVQZ	-23.34	+4.76	-4.11	+0.26	[-0.10]	[-0.05]	[-22.58]
aV5Z	-23.33	+4.80	-4.08	+0.25	[-0.10]	[-0.05]	[-22.51]
CBS Limit	[-23.34]	[+4.83]	[-4.05]	[+0.25]	[-0.10]	[-0.05]	[-22.46]

ΔH_{0K} = -22.31 + 0.63 – 0.15 + 0.08 – 0.02 – 0.00 = **-21.77 kcal mol^{-1}**

Table : Example focal point table for products (C_2H_2 + NCO) relative to reactants (C_2H + HNCO) in kcal mol^{-1}. A three-point extrapolation scheme is used to estimate the CBS limit for the SCF energies, and a two-point extrapolation is used to extrapolate post Hartree-Fock energies.

Bond Orders

Isomer	Bond	Bond Order
Butterfly	Pb–Pb	0.70
	Pb–H	0.39
Planar	Pb–Pb	0.69
	Pb–H	0.38
Monobridged	Pb–Pb	0.81
	Pb–H (1)	0.39
	Pb–H (2)	0.39
	Pb–H (3)	0.45
Vinylidene-like	Pb–Pb	0.88
	Pb–H	0.90
Trans	Pb–Pb	0.57
	Pb–H	0.84
Cis	Pb–Pb	0.54
	Pb–H	0.84
Linear	Pb–Pb	2.32
	Pb–H	0.88

Table 3: Wiberg Bond Order of each Pb-Pb and Pb-H bond.

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