Dialane Anion: Three-Center Two-Electron or Two-Center One-Electron Bonded

Shan Xi Tian

Hefei National Laboratory for Physical Sciences at Microscale, Laboratory of Bond Selective Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic China

Supplementary Materials:

TABLE 1S: Natural Bond Analysis of the Selected Natural Bonds.^a

		Hybrid Composition	Occupancy	Energy(au)
$\text{Al}_2\text{H}_6(D_{2h})$	Al—H _b —Al	$0.8488(\text{sp}^{0.02})_{\text{Hb}} + 0.3738(\text{sp}^{6.63}\text{d}^{0.05}\text{f}^{0.01})_{\text{Al}} \times 2$	1.96346	-0.56559
$\text{Al}_2\text{H}_6^-(D_{3d})$	Al—Al	$\alpha: 0.7071(\text{sp}^{4.07}\text{d}^{0.07}\text{f}^{0.02})_{\text{Al}} \times 2$ $\beta: \text{-----}$	$\alpha: 0.95814$ $\beta: \text{-----}$	$\alpha: -0.19647$ $\beta: \text{-----}$
$\text{Al}_2\text{H}_6^-(C_s)$	Al—H _b —Al	$\alpha: 0.8694s_{\text{Hb}} + 0.3403(\text{sp}^{7.40}\text{d}^{0.08}\text{f}^{0.01})_{\text{Al1}}$ $+ 0.3583(\text{sp}^{6.44}\text{d}^{0.06}\text{f}^{0.01})_{\text{Al2}}$ $\beta: 0.8760s_{\text{Hb}} + 0.3423(\text{sp}^{4.11}\text{d}^{0.05})_{\text{Al1}}$ $+ 0.3399(\text{sp}^{6.72}\text{d}^{0.06}\text{f}^{0.01})_{\text{Al2}}$	$\alpha: 0.98980$ $\beta: 0.98732$	$\alpha: -0.39208$ $\beta: -0.39169$

^a Calculated at the HF/6-311++G(2df,2p) // CCSD/6-311++G(2df,2p) level.

TABLE 2S: Natural Atomic Populations Predicted at the HF/6-311++G(2df,2p) // CCSD/6-311++G(2df,2p) Level.

		Natural Atomic Population
$\text{Al}_2\text{H}_6(D_{2h})$	Al	1.17837
	H _b	-0.42247
	H _t	-0.37795
$\text{Al}_2\text{H}_6^-(D_{3d})$	Al	0.87435
	H _t	-0.45812
$\text{Al}_2\text{H}_6^-(C_s)$	Al1	0.70307
	Al2	1.06898
	H _b	-0.51263
	H1 _t	-0.46598
	H2 _t	-0.44513
	H3 _t	-0.43719

TABLE 3S: Energetics (au) of the Fragments

		Energy +ZPVE	Enthalpy
AlH ₂ (C _{2v})	MP2/6-311++G(d,p)	-243.075841	-243.071983
	MP2/6-311++G(2df,2p)	-243.086226	-243.082367
	CCSD-T/6-311++G(2df,2p) ^a	-243.1179269	
AlH ₂ ⁻ (C _{2v})	MP2/6-311++G(d,p)	-243.097809	-243.093961
	MP2/6-311++G(2df,2p)	-234.114793	-243.110940
	CCSD-T/6-311++G(2df,2p) ^a	-243.153288	
AlH ₃ (D _{3h})	MP2/6-311++G(d,p)	-243.697925	-243.693906
	MP2/6-311++G(2df,2p)	-243.710320	-243.706293
	CCSD-T/6-311++G(2df,2p) ^a	-243.755567	
AlH ₃ ⁻ (C _{3v})	MP2/6-311++G(d,p)	-243.701205	-243.697129
	MP2/6-311++G(2df,2p)	-243.718176	-243.714089
	CCSD-T/6-311++G(2df,2p) ^a	-243.764785	
AlH ₄ (C _s) ^b	MP2/6-311++G(d,p)	-244.223988	-244.218735
	MP2/6-311++G(2df,2p)	-244.237757	-244.232656
	CCSD-T/6-311++G(2df,2p) ^a	-244.291598	
AlH ₄ ⁻ (T _d)	MP2/6-311++G(d,p)	-244.323468	-244.319297
	MP2/6-311++G(2df,2p)	-244.342279	-244.338092
	CCSD-T/6-311++G(2df,2p) ^a	-244.401943	

^a Over the CCSD/6-311++G(2df,2p) geometries. ^b One imaginary vibrational frequency is predicted: *i*69.05 cm⁻¹ at the UMP2/6-311++G(d,p) level; *i*37.85cm⁻¹ at the UMP2/6-311++G(2df,2p) level. Energies of AlH₄(C_i) are -244.223990 au, -244.237709 au, and -244.291596 au predicted at the UMP2 / 6-311++G(d,p), UMP2 / 6-311++G(2df,2p), and UCCSD-T/6-311++G(2df,2p) // UCCSD/6-311++G(2df,2p) levels, respectively.

TABLE 4S: Natural Bond Orbital Analysis of the Selected (α) Orbitals Calculated at the UHF / 6-311++G(2df,2p) // UCCSD / 6-311++G(2df,2p) level

		E(2) ^a (kcal/mol)	δε (au) ^a	F _{ij} (au) ^a
Al ₂ H ₆ ⁻ (D _{3d})	σ _{Al•Al} → σ* _{Al-H_f}	1.82	0.70	0.046
Al ₂ H ₆ ⁻ (C _s)	n _{AlI} → σ* _{Al-H_b-Al}	2.84	0.56	0.051
	n _{AlI} → Ry _{H_b} ^b	2.34	0.78	0.054

^a. Notation can be found in Ref. 16. ^b The Rydberg orbital of H_b atom.

SCHEME: Diagram of the transition between two anionic isomers, calculated at the MP2/6-311++G(2df,2p) level.

Cartesian Coordinates Optimized at the CCSD/6-311++G(2df,2p) Level.

$\text{Al}_2\text{H}_6(D_{2h})$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	1.998006	1.414931	0.000000
2	1	0	1.998006	-1.414931	0.000000
3	1	0	-1.998006	1.414931	0.000000
4	1	0	-1.998006	-1.414931	0.000000
5	1	0	0.000000	0.000000	1.145783
6	1	0	0.000000	0.000000	-1.145783
7	13	0	1.306374	0.000000	0.000000
8	13	0	-1.306374	0.000000	0.000000

$\text{Al}_2\text{H}_6^-(D_{3d})$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	1	0	0.000000	1.572218	1.849039
2	1	0	1.361581	-0.786109	1.849039
3	1	0	-1.361581	-0.786109	1.849039
4	1	0	1.361581	0.786109	-1.849039
5	1	0	0.000000	-1.572218	-1.849039
6	1	0	-1.361581	0.786109	-1.849039
7	13	0	0.000000	0.000000	1.475084
8	13	0	0.000000	0.000000	-1.475084

Al₂H₆⁻(C_s)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	0.785189	1.900797	1.369990
2	1	0	0.785189	1.900797	-1.369990
3	1	0	-0.723988	-2.116628	-1.354285
4	1	0	1.567018	-1.574985	0.000000
5	1	0	-0.723988	-2.116628	1.354285
6	1	0	-0.554701	0.085381	0.000000
7	13	0	-0.043643	1.704137	0.000000
8	13	0	-0.043643	-1.556347	0.000000

AlH₂(C_{2v})

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	13	0	0.000000	0.000000	0.108973
2	1	0	0.000000	1.373230	-0.708326
3	1	0	0.000000	-1.373230	-0.708326

AlH₂⁻(C_{2v})

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	13	0	0.000000	0.000000	0.152324
2	1	0	0.000000	1.247757	-0.990108
3	1	0	0.000000	-1.247757	-0.990108

AlH₃(D_{3h})

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	13	0	0.000000	0.000000	0.000000
2	1	0	0.000000	1.583416	0.000000
3	1	0	1.371279	-0.791708	0.000000
4	1	0	-1.371279	-0.791708	0.000000

$\text{AlH}_3^-(C_{3h})$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	0.000000	1.563894	-0.383782
2	1	0	-1.354372	-0.781947	-0.383782
3	1	0	1.354372	-0.781947	-0.383782
4	13	0	0.000000	0.000000	0.088565

$\text{AlH}_4(C_s)$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	13	0	0.000000	0.301001	0.000000
2	1	0	0.751179	0.002474	1.374788
3	1	0	-1.101642	-1.825202	0.000000
4	1	0	0.751179	0.002474	-1.374788
5	1	0	-0.400717	-2.092757	0.000000

$\text{AlH}_4(C_I)$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	13	0	-0.282171	-0.000162	-0.107198
2	1	0	-0.269725	-1.372335	0.705570
3	1	0	2.101546	-0.012791	-0.379296
4	1	0	-0.264981	1.377204	0.696692
5	1	0	2.101389	0.010025	0.370612

$\text{AlH}_4^-(T_d)$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	13	0	0.000000	0.000000	0.000000
2	1	0	0.949998	0.949998	0.949998
3	1	0	-0.949998	-0.949998	0.949998
4	1	0	-0.949998	0.949998	-0.949998
5	1	0	0.949998	-0.949998	-0.949998