Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information For

Aluminum chain in $Li_2Al_3H_8^-$ as suggested by photoelectron spectroscopy and ab initio calculations

Ivan A. Popov,‡[a] Xinxing Zhang,‡[b] Bryan W. Eichhorn,[c] Alexander I. Boldyrev,*[a] and Kit H. Bowen*[b]

[a] *Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322, USA, E-mail: a.i.boldyrev@usu.edu*

[b] *Departments of Chemistry and Materials Science, Johns Hopkins University, Baltimore, MD 21218, USA, E-mail: kbowen@jhu.edu*

[c] *Department of Chemistry and Biochemistry, University of Maryland at College Park, College Park, MD 20742, USA*

‡These authors contributed equally.

Table of Contents

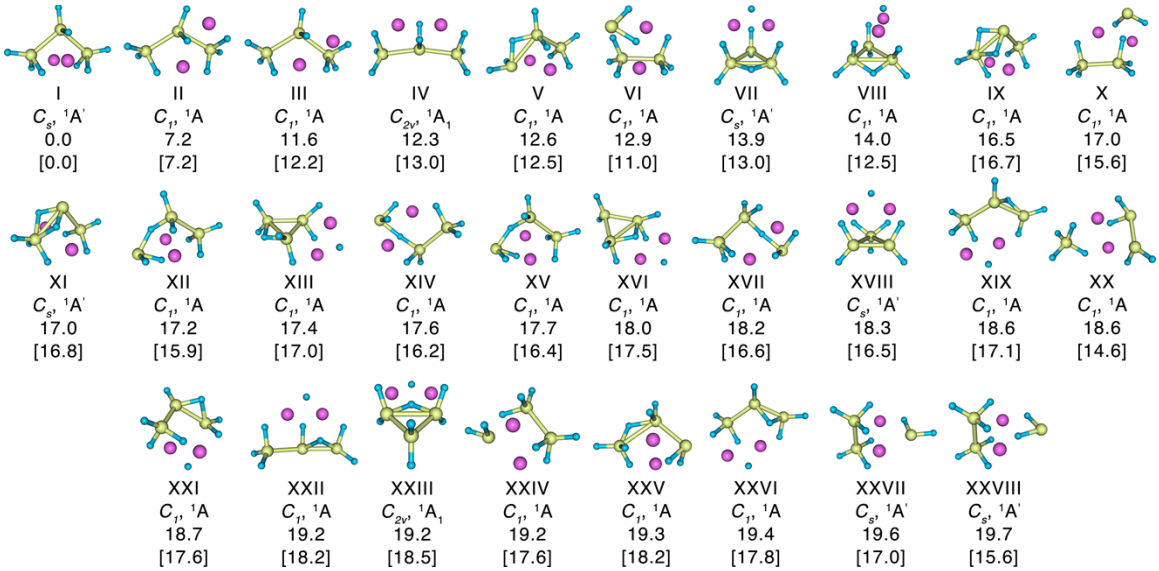

Figure S1. Optimized isomers of $Li_2Al_3H_8^-$ (Δ=20 kcal/mol), their point group symmetries, spectroscopic states, and ZPE corrected relative energies at the PBE0/6-311++G(d, p) and CCSD(T)/aug-cc-pVTZ//PBE0/6-311++G(d, p) (in square brackets) levels of theory.

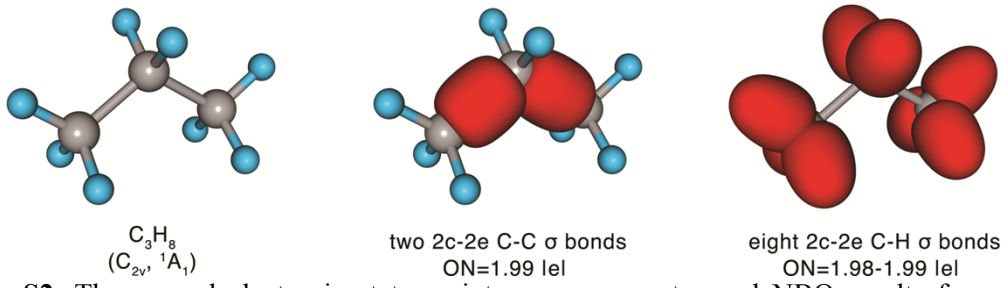

Figure S2. The ground electronic state, point group symmetry and NBO results for propane molecule: two 2c-2e C-C σ bonds (center, shown superimposed) and eight 2c-2e C-H σ bonds (right, shown superimposed).

Table S1. The Cartesian coordinates of global minimum structure and low-lying isomers of $Li_2Al_3H_8^-$ at the PBE0/6-311++G(d, p) level of theory.

	I		
3	1.425579000	-1.166947000	0.000000000
3	-1.750060000	-0.439370000	0.000000000
13	0.053047000	-0.402754000	2.054612000
13	0.053047000	-0.402754000	-2.054612000
13	0.053047000	1.321395000	0.000000000
1	-1.642792000	1.404974000	0.000000000
1	-1.345446000	-1.258589000	-1.618130000
1	0.726492000	2.789577000	0.000000000
1	-1.345446000	-1.258589000	1.618130000
1	1.216134000	-1.610730000	1.733478000
1	1.216134000	-1.610730000	-1.733478000

1	0.039761000	-0.171751000	3.653971000
1	0.039761000	-0.171751000	-3.653971000
		II	
3	1.817652000	1.672445000	0.899593000
3	-0.049617000	-1.077060000	1.276097000
13	2.115961000	-0.622075000	-0.242574000
13	-2.430693000	-0.287474000	-0.069019000
13	-0.112616000	0.888935000	-0.328184000
1	3.065023000	-1.355498000	-1.328040000
1	0.549607000	2.435828000	-0.335535000
1	-3.586983000	0.494467000	0.767760000
1	-1.797852000	-1.459492000	1.001655000
1	-3.020747000	-1.103933000	-1.343611000
1	3.108800000	0.431303000	0.680513000
1	0.286561000	0.792605000	1.422264000
1	1.647012000	-1.753450000	0.925021000
		III	
3	-0.148519000	-0.954683000	1.243810000
3	1.980949000	0.687786000	1.615210000
13	-0.113417000	1.035374000	-0.276377000
13	-2.372260000	-0.360036000	-0.073983000
13	2.077923000	-0.519004000	-0.412047000
1	-2.858549000	-1.193912000	-1.384931000
1	-3.613308000	0.387425000	0.674472000
1	2.801199000	-1.610982000	-1.349800000
1	0.232826000	1.001717000	1.498433000
1	-1.825623000	-1.536358000	1.051782000
1	3.276993000	0.382274000	0.405174000
1	0.095017000	2.580613000	-0.722071000
1	1.694961000	-1.242435000	1.161184000
		IV	
3	0.000000000	1.452253000	-1.894542000
3	0.000000000	-1.452253000	-1.894542000
13	0.000000000	-2.637253000	0.443168000
13	0.000000000	2.637253000	0.443168000
13	0.000000000	0.000000000	0.056869000
1	-1.355708000	-3.271985000	1.073528000
1	1.124179000	0.000000000	-1.375952000
1	1.355708000	3.271985000	1.073528000
1	-1.124179000	0.000000000	-1.375952000
1	1.355708000	-3.271985000	1.073528000
1	0.000000000	-3.092263000	-1.218311000
1	0.000000000	3.092263000	-1.218311000
1	-1.355708000	3.271985000	1.073528000

		V	
3	-0.116555000	-1.700334000	-0.883211000
3	0.083774000	-0.208861000	1.817868000
13	0.056462000	1.355669000	-0.214475000
13	-2.064315000	-0.506016000	0.111414000
13	2.001039000	-0.474687000	-0.030287000
1	1.657253000	-1.926856000	-0.818625000
1	3.549370000	-0.117345000	-0.330056000
1	-3.654306000	-0.171201000	0.120332000
1	-1.547208000	0.974766000	-0.765168000
1	0.263283000	2.758863000	-1.000955000
1	1.810640000	-0.861603000	1.597179000
1	-0.056121000	1.639610000	1.437212000
1	-1.835973000	-1.443216000	-1.310369000
		VI	
3	0.289192000	-1.398764000	-0.905229000
3	-0.156794000	-0.285339000	1.792608000
13	2.532118000	-0.364118000	0.049450000
13	-2.078662000	-0.570939000	-0.067699000
13	-0.257231000	1.378145000	-0.166685000
1	-1.486911000	-1.896185000	-0.914850000
1	0.075723000	1.510502000	1.475219000
1	1.063113000	-1.100019000	0.810572000
1	-3.663858000	-0.425848000	-0.340197000
1	2.036776000	-1.383619000	-1.287478000
1	1.270010000	0.800002000	-0.702791000
1	-1.823303000	-1.049399000	1.536660000
1	-0.419662000	2.836730000	-0.835132000
		VII	
3	0.495336000	2.044301000	1.236266000
3	0.495336000	2.044301000	-1.236266000
13	-1.446110000	0.302707000	0.000000000
13	0.495336000	-0.668353000	1.420195000
13	0.495336000	-0.668353000	-1.420195000
1	1.242584000	3.061313000	0.000000000
1	-3.036424000	0.065708000	0.000000000
1	1.483524000	-1.106719000	0.000000000
1	-1.077316000	1.944692000	0.000000000
1	1.481647000	0.578523000	-1.933371000
1	1.481647000	0.578523000	1.933371000
1	0.686501000	-1.972928000	-2.347315000
1	0.686501000	-1.972928000	2.347315000
		VIII	
3	0.622787000	-1.474212000	1.855994000
3	1.610256000	0.899889000	1.739471000

13	1.051719000	-0.812913000	-0.817336000
13	-1.588035000	-0.438596000	0.117313000
13	-0.019584000	1.566631000	-0.207656000
1	1.520524000	-1.943563000	0.321375000
1	0.585715000	2.267616000	1.180613000
1	1.570411000	-0.400171000	2.883925000
1	-3.070004000	-0.940675000	-0.298133000
1	-1.158238000	-1.246264000	1.518557000
1	-0.596259000	-1.483948000	-0.935795000
1	0.005590000	2.636680000	-1.415945000
1	1.669832000	-1.263301000	-2.241150000
		IX	
3	-0.077605000	-2.186142000	-0.481405000
3	0.092014000	-0.379480000	1.787191000
13	-1.723087000	-0.410890000	-0.093876000
13	-0.002133000	1.659547000	-0.123628000
13	1.828452000	-0.340605000	-0.115931000
1	-0.998396000	-1.616497000	1.052405000
1	-0.996888000	0.924864000	1.164046000
1	1.833505000	-0.712674000	1.553291000
1	3.334439000	0.053898000	-0.547550000
1	-1.344990000	1.064006000	-1.057337000
1	1.624379000	-1.914631000	-0.747022000
1	-1.555423000	-1.591489000	-1.308683000
1	-3.281879000	-0.315285000	0.308140000
		X	
3	0.228795000	-1.378580000	0.111909000
3	1.544850000	0.922893000	1.403293000
13	-0.528739000	1.271769000	-0.218204000
13	-2.365557000	-0.633255000	0.043906000
13	2.674032000	-0.621668000	-0.291284000
1	-3.291106000	-0.840112000	-1.274509000
1	1.668506000	-0.962746000	1.187667000
1	0.077422000	1.919389000	1.220556000
1	-0.459863000	2.467516000	-1.302430000
1	1.019958000	0.375626000	-0.532869000
1	3.172538000	0.753674000	0.602584000
1	-3.217541000	-0.524553000	1.424358000
1	-1.427418000	-2.040732000	0.181602000

Table S2. X-X-X valence angle values (deg.) of propane and X-homocatenated propane-like species (X=B, Al, Ga).

C_3H_8[a]	$Li_3B_3H_8$[b]	$Li_2Al_3H_8^-$[a]	$Li_2Al_3H_8$[a]	$Li_3Al_3H_8$[c]	$Cs_{10}H[Ga_3H_8]_3$[d]
112.8	116.0	100.0	90.7	92.5	120.1

[a] Calculated at the PBE0/6-311++G(d, p) levels of theory.
[b] From ref. 6.
[c] From ref. 16.
[d] From ref. 9.

Table S3. The observed vertical detachment energies (VDEs) for $Li_2Al_3H_8^-$ and comparison with calculated VDEs for isomers **I** (C_s, $^1A'$) and **II** (C_1, ^1A) at three levels of theory. All energies are in eV.

Feature	VDE (Expt.)	Final state and electronic configuration	VDE (Theor.)		
			TD-DFT[a]	OVGF[b]	CCSD(T)[c]
		Isomer **I** (C_s, $^1A'$)			
X	2.70	$^2A''\ldots(2a'')^2(4a')^2(3a'')^2(5a')^2(6a')^2(4a'')^1$	2.67	2.61	2.78
A	4.32	$^2A'\ldots(2a'')^2(4a')^2(3a'')^2(5a')^2(6a')^1(4a'')^2$	4.14	4.21	4.21
		$^2A'\ldots(2a'')^2(4a')^2(3a'')^2(5a')^1(6a')^2(4a'')^2$	5.72	6.24	-[d]
		$^2A''\ldots(2a'')^2(4a')^2(3a'')^1(5a')^2(6a')^2(4a'')^2$	5.60	6.51	-[d]
		$^2A'\ldots(2a'')^2(4a')^1(3a'')^2(5a')^2(6a')^2(4a'')^2$	5.98	6.80	-[d]
		$^2A''\ldots(2a'')^1(4a')^2(3a'')^2(5a')^2(6a')^2(4a'')^2$	6.11	6.89	-[d]
		Isomer **II** (C_1, ^1A)			
X	2.70	$^2A\ldots(5a)^2(6a)^2(7a)^2(8a)^2(9a)^2(10a)^1$	2.82	2.81	2.94
A	4.32	$^2A\ldots(5a)^2(6a)^2(7a)^2(8a)^2(9a)^1(10a)^2$	4.19	4.28	-[d]
		$^2A\ldots(5a)^2(6a)^2(7a)^2(8a)^1(9a)^2(10a)^2$	5.00	5.89	-[d]
		$^2A\ldots(5a)^2(6a)^2(7a)^1(8a)^2(9a)^2(10a)^2$	5.42	6.18	-[d]
		$^2A\ldots(5a)^2(6a)^1(7a)^2(8a)^2(9a)^2(10a)^2$	5.68	6.51	-[d]
		$^2A\ldots(5a)^1(6a)^2(7a)^2(8a)^2(9a)^2(10a)^2$	6.20	6.94	-[d]

[a]VDEs were calculated at the TD-PBE0/aug-cc-pVTZ//PBE0/6-311++G(d, p) level of theory. The first VDE was calculated as the energy difference between the ground electronic state of the anion and the lowest doublet electronic state of the neutral at the geometry of the anion. Vertical excitation energies from the neutral states were then calculated and added to the first VDE to approximate the higher VDEs. (S^2 values did not exceed their normal values by more than 2%).
[b]VDEs were calculated at the OVGF/6-311++G(d, p)//PBE0/6-311++G(d, p) level of theory through the corrections to the orbital energies due to electron correlation and electron relaxation. (Polestrength values were found to be more than 0.86).
[c]VDEs were calculated at the CCSD(T)/aug-cc-pVTZ//PBE0/6-311++G(d, p) level of theory (NORM(A) values were found to be 1.14).
[d]A value was not able to be calculated at this level of theory.

Table S4. Comparison of geometrical characteristics of $Li_2Al_3H_8^-$ and its neutral species at the PBE0/6-311++G(d, p) level of theory.

Bond lengths (Å) and the valence angle (deg.)	$Li_2Al_3H_8^-$	$Li_2Al_3H_8$
∠(Al-Al-Al)	100.0	90.7
R(Al-Al)	2.68	2.75
R(Li-Li)	3.26	3.81
$R(Al_3\text{-}H_9)$	1.70	1.65
$R(Al_3\text{-}H_{12})$	1.62	1.59
$R(Al_3\text{-}H_{10})$	1.71	1.65
$R(Al_5\text{-}H_6)$	1.70	1.67
$R(Al_5\text{-}H_8)$	1.62	1.59

Table S5. NPA charges on atoms of the global minimum structure **I** of $Li_2Al_3H_8^-$ at the PBE0/6-311++G(d, p) level of theory.

Atoms	NPA charge
Li_1	0.56241
Li_2	0.48642
Al_3	0.35786
Al_4	0.35786
Al_5	-0.02440
H_6	-0.32309
H_7	-0.35567
H_8	-0.29729
H_9	-0.35567
H_{10}	-0.38540
H_{11}	-0.38540
H_{12}	-0.31882
H_{13}	-0.31882