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

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Dialane anions can be formed via a single three-center two-electron (3c−2e) or two-center one-electron (2c−1e) bond. The 2c−1e bonded anion $Al_2H_6^-(D_{3d})$ and the 3c-2e bonded anion $Al_2H_6^-(C_s)$ have significant thermodynamic stabilities with respect to the neutral $Al_2H_6(D_{2h})$ and correspond to 0.22 and 0.32 eV of the adiabatic electron affinities, respectively. In particular, the 2c−1e bond plays an essential role in stabilizing the $Al_2H_6^-(D_{3d})$ anion.

Boron hydrides have been investigated widely, due to the unique three-center two-electron (3c−2e) bonding and the extensive application in chemistry.[1] Dialane (Al_2H_6), an isostructural compound of diborane (B_2H_6), was recently isolated,[2] and its stability was theoretically examined a decade ago.[3] The radical cations $B_2H_6^+$ and $Al_2H_6^+$ were detected as the trace in the mass spectrometer, indicating their less stabilities with respect to the other fragments.[4,5] On the other hand, only one report, to our knowledge, focused on the photodetachment of the $Al_2H_6^-$ anion;[6] AlH_4^- was studied with the infrared matrix isolation methods.[1,2b,7]

The radical anions may exhibit the dramatic geometrical changes with respect to the neutral. As far as the stable $Al_2H_6^-$ anion, it has been predicted to be a singly Al−H_b−Al bridging (3c−2e bonded) radical (C_s symmetry) in which the bridging hydrogen atom (H_b) is negatively charged.[6] When we search the possibility of the other stable radicals beginning with the neutral D_{2h} symmetrical geometry, the anion at D_{2h} symmetry is proved to be at a high-order saddle point having three imaginary vibrational frequencies. The C_s symmetric one can be reached along a vibrational mode of the imaginary frequencies, whereas the other two lead to a D_{3d} symmetrical radical in which two aluminum atoms are one-electron (namely, two-center one-electron, 2c−1e) bonded. The former is slightly more stable than the latter. Until now, no other 2c−1e bonded anionic species has been known. Moreover, Pluta et al. found that the Al═Al π bond could be further stabilized by an additional electron.[8] A typical 2c−1e bonded anion $Al_2H_6^-(D_{3d})$ is computed to be stable for the first time. It is informative to investigate their structural and thermodynamic properties, in view of the great interest on the electron-deficient molecules in free-radical chemistry and biochemistry.[9] The results presented in this Letter are hopefully to be reasonable guidance for spectroscopists to research the unusual species.

Considering the specific bonds in the species, we used the second-order perturbation MP2 method and 6-311++G(d,p) and 6-311++G(2df,2p) basis sets to optimize the geometrical parameters. They were further re-optimized with the coupled-cluster CCSD theory. The coupled-cluster including single, double, and triple excitations (CCSD-T) theory was employed in the extrapolated energetic calculations over the CCSD optimized geometries. The vertical and adiabatic electron affinities (EA_v and EA_a) of the neutral and the vertical detachment energies (VDEs) of the stable anions were calculated. The partial third-order quasiparticle approximation of electron propagator theory (P3)[10] was also used to obtain the EA_v and VDE values. No serious spin contamination ($\langle S\rangle^2 < 0.76$) was found for the spin-unlimited HF reference states used in the MP2, CCSD, CCSD-T, and P3 calculations. All calculations were carried out with Gaussian 98 package.[11] Bond characteristics were analyzed by natural bond orbital (NBO) theory.[12] Electron density maps of the single occupied molecular orbitals (SOMOs) of the anions were plotted at the contour values ±0.03, using the MOLDEN graphics program.[13]

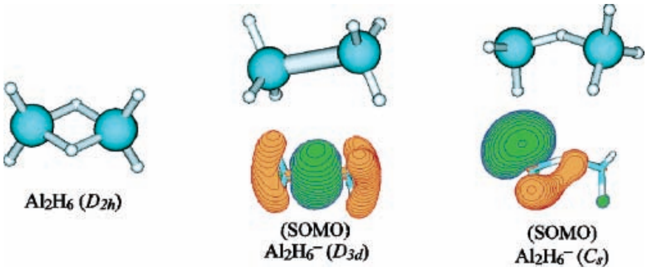

Figure 1. Molecular structure of dialane and anions.

The optimized geometries are shown in Figure 1, where the conformer $Al_2H_6^-(C_s)$ is similar to that predicted with the density functional BPW91 method.[6] The Al···Al distance in $Al_2H_6(D_{2h})$ is optimized to be 2.6081, 2.6069, and 2.6128 Å at the MP2/6-311++G(d,p), MP2/6-311++G(2df,2p), and CCSD/6-311++G(2df,2p) levels, respectively. They are close to the results reported previously.[6,3d] No Al−Al bond is formed in Al_2H_6 according to the NBO analysis. $Al_2H_6^-(D_{3d})$ is structurally similar to ethane, but the aluminum bond (Al•Al) is weak and predicted to be much longer than the Al_2 bond of 2.86 Å.[6] Basis set and electron correlation dependencies in the calculations can

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TABLE 1: Geometrical Parameters (Length in Å; Angle in Degree) of Dialane Anions

		MP2		CCSD
		6-311++G(d,p)	6-311++G(2df,2p)	6-311++G(2df,2p)
D_{3d}	Al−Al	2.9376	2.9585	2.9502
	Al−H_t	1.6085	1.6114	1.6161
	H_t−Al−Al	103.43	103.38	103.38
C_s	Al···Al	3.2594	3.2508	3.2605
	Al−H_t	1.6041	1.6075	1.6132
		1.6087	1.6115	1.6158
		1.6035	1.6065	1.6108
	Al−H_b	1.6914	1.6928	1.6975
		1.7121	1.7146	1.7194
	Al−H_b−Al	146.54	145.14	145.19

TABLE 2: Infrared Active Vibrational Frequencies (cm^{-1}) and Intensities (km/mol) Predicted at the MP2/6-311++G(2df,2p) Level

$Al_2H_6(D_{2h})$			$Al_2H_6^-$			
			D_{3d}		C_s	
b_{1u}:	651(304)	632(0.039)[a]	a_{2u}:	685(1364)	a′:	116(1)
	1312(362)	1268(0.053)[a]		1834(254)		383(13)
b_{2u}:	223(17)		e_u:	216(17)		560(296)
	879(229)	836(0.037)[a]		791(785)		741(359)
	2021(406)	1932(0.069)[a]		1823(1837)		771(695)
b_{3u}:	730(678)	702(0.048)[a]				792(220)
	1534(1155)	1408(0.128)[a]				876(177)
	2001(124)	1915(0.023)[a]				1811 (1131)
						1851(498)
						1929(653)
					a″:	38(2)
						128(0)
						493(2)
						780(10)
						806(317)
						1816(250)
						1836(662)

[a] From the matrix infrared spectra.[2]

TABLE 3: Vertical and Adiabatic Electron Affinities (EA_v and EA_a in eV) of Dialane and Vertical Detachment Energies (VDEs in eV) of the Anions

methods	EA_v	EA_a		VDE	
		D_{3d}	C_s	D_{3d}	C_s
MP2/6-311++G(d,p)	−0.79	0.11[a]	0.25[a]	3.08	2.22
MP2/6-311++G(2df,2p)	−0.67	0.26[a]	0.35[a]	3.19	2.32
CCSD-T/6-311++G(2df,2p)[b]	−0.52	0.22	0.32	3.23	2.38
P3/6-311++G(2df,2p)[b]	−0.66			3.28	2.34
BPW91/6-311G**[6]			0.44		2.42
experimental[6]					2.4 ± 0.15

[a] With the zero-point vibrational energy corrections. [b] Over the CCSD/6-311++(2df,2p) optimized geometries.

be found by comparison of the geometrical parameters listed in Table 1. The stabilities of the anionic species are examined by the analytical vibrational frequency calculations. The infrared active vibrational frequencies are summarized in Table 2, in particular, the 2c−1e Al•Al bond stretching frequency is 192 cm^{-1} (a_{1g}) without infrared activity for $Al_2H_6^-(D_{3d})$. Good agreement between the calculated infrared vibrational frequencies and the experimental data[2] for $Al_2H_6(D_{2h})$ demonstrates the reliability of the present calculations.

Hybrids, occupancies, and energies of the 3c−2e bonds Al−H_b-Al in $Al_2H_6(D_{2h})$ and $Al_2H_6^-(C_s)$ and the singly occupied 2c−1e bond Al•Al in $Al_2H_6^-(D_{3d})$ are presented in Table 1S (see the Supporting Information). The 3c−2e bond in $Al_2H_6^-(C_s)$ is weakened with respect to that in the neutral, exhibiting the higher energy levels. Moreover, natural atomic population analyses in Table 2S show that both H_b and H_t (terminal H) atoms are negatively charged, whereas two aluminum atoms in the anions are still positively charged. In $Al_2H_6^-(C_s)$, two aluminum atoms have the distinctly different negative charges, namely, the attached electron is mostly on one of the aluminum atoms as shown in Figure 1. The electron is localized between two aluminum atoms in $Al_2H_6^-(D_{3d})$, which leads to the significant decrease of the positive charges of the aluminum atoms.

The transition state between these two anionic isomers is calculated with 0.26 eV higher than the D_{3d} anion and 0.35 eV higher than the C_s anion (see Scheme in the Supporting Information), predicted at the MP2/6-311++G(2df,2p) level. Transition to the former can occur by breaking the single 3c−2e bond of the latter, and the low energetic barrier permits the considerable possibility of transition. It is interesting that this transition state is almost at the energetic level of the neutral $Al_2H_6(D_{2h})$.

As shown in Table 3, the EA_v values are negative; namely, formation of the anion by electron attachment is endothermic. However, the positive EA_a values for theses two anions indicate the thermodynamic stabilities, suggesting they could be detected in the mass spectrometer. The photodetachment spectrum using the mass spectrometry technique to select the $Al_2H_6^-$ clusters gave the VDE of 2.4 ± 0.15 eV, which was assigned to the $Al_2H_6^-(C_s)$ conformer only.[6]

The CCSD-T and P3 results (2.38 and 2.34 eV) for $Al_2H_6^-(C_s)$ are in good agreement with the experimental datum. EA_a values demonstrate that the D_{3d} symmetrical anion is less stable by 0.1 eV than the C_s one, but the higher VDE 3.23 eV of the former is predicted. Correspondingly, the structureless band with the binding energies higher than 3 eV was observed.[6] The next single electron detachment energy around 6 eV predicted at the P3/6-311++G(2df,2p) level is related to the higher singlet or triplet state of the neutral. Two anions are suspected to coexist in the experiment, supported by their comparable stabilities with respect to the neutral and the low energetic transition barrier discussed above. There may be considerable vertical (Franck−Condon) transitions of $Al_2H_6^-(C_s)$

TABLE 4: Dissociation Energy (Δ*E* in eV) and Enthalpy Change (Δ*H* in eV)

	Δ*E*		Δ*H*(MP2)	
	MP2[a]	CCSD-T[b]	6-311++G(d,p)	6-311++G(2df,2p)
$Al_2H_6 \rightarrow 2AlH_3(D_{3h})$	−1.40	−1.60	−1.42	−1.46
$Al_2H_6^-(D_{3d}) \rightarrow 2AlH_3(D_{3h}) + e^-$	−1.66	−1.82	−1.49	−1.68
$\rightarrow AlH_3(D_{3h}) + AlH_3^-(C_{3v})$	−1.45	−1.57	−1.40	−1.47
$Al_2H_6^-(C_s) \rightarrow 2AlH_3(D_{3h}) + e^-$	−1.76	−1.91	−1.64	−1.78
$\rightarrow AlH_3(D_{3h}) + AlH_3^-(C_{3v})$	−1.65	−1.66	−1.55	−1.57
$\rightarrow AlH_2(C_{2v}) + AlH_4^-(T_d)$	−1.54	−1.68	−1.54	−1.56
$\rightarrow AlH_4(C_s) + AlH_2^-(C_{2v})$	−3.61	−3.72	−3.88	−3.66

[a] Using the 6-311++G(2df,2p) basis set and including the zero-point-vibrational energy corrections. [b] Over the CCSD/6-311++G(2df,2p) geometries.

→ $Al_2H_6(D_{2h})$ + e^- due to the structural common (3c−2e bond). The conventional Franck−Condon factor for $Al_2H_6^-(D_{3d})$ → $Al_2H_6(D_{2h})$ + e^- is meaningless because of the remarkable geometrical differences between $Al_2H_6^-(D_{3d})$ and $Al_2H_6(D_{2h})$ and the purely repulsive potential surface of the neutral dialane at D_{3d} symmetry (see the following discussion); however, this case can be simulated by reflection principle, which holds for transitions between bound and continuum states.[14] The other dissociative detachments of the anions should be considered to assign the spectrum beyond 3 eV. Thereby, thermodynamic stabilities of the anions are discussed in the following text.

Possible fragments such as AlH_2, AlH_3, AlH_4, and their anions are optimized and the stabilities are checked through the harmonic vibrational frequency calculations.[15] EA_a values for AlH_2, AlH_3, and AlH_4 are predicted to be 0.96, 0.25, and 3.00 eV, respectively. It is noted that EA_a of Al_2H_6 is extremely close to that of AlH_3, due to the attached electron is dominantly around the aluminum atom(s) in the anions. Table 4 lists dissociation energies (ΔE) and enthalpy changes (ΔH) of the possible fragmentations. The dimerization energy of Al_2H_6 is 1.60 eV, which is close to 1.55 eV at the CCSD/DZP level.[3d] The most energetically favorable dissociation of the D_{3d} anion is to be $AlH_3(D_{3h})$ + $AlH_3^-(C_{3v})$, rather than $2AlH_3(D_{3h})$ + e^-; that of the C_s anion is either to be $AlH_3(D_{3h})$ + $AlH_3^-(C_{3v})$ or $AlH_2(C_{2v})$ + $AlH_4^-(T_d)$. In $Al_2H_6^-(C_s)$ → $AlH_2(C_{2v})$ + $AlH_4^-(T_d)$, the attached electron is expected to transfer from the AlH_2^- moiety to the AlH_4 moiety (see Figure 1). Significant hyperconjugative interactions, $\sigma_{Al\bullet Al} \rightarrow \sigma^*_{Al-H_t}$ in $Al_2H_6^-(D_{3d})$ and $n_{Al} \rightarrow \sigma^*_{Al-H_b-Al}$ in $Al_2H_6^-(C_s)$, exhibiting the second-order energies[16] in the NBO theorem 1.82 and 2.84 kcal/mol, control the staggered conformal preferences[17] and the potential dissociations. All dissociations are endothermic, but smaller than 2 eV, except for $Al_2H_6^-(C_s)$ → $AlH_2^-(C_{2v})$ + $AlH_4(C_s)$. In the experiment,[6] the UV laser (4.66 eV) is high enough to have the most anions as well as the neutral Al_2H_6 dissociated. Moreover, the dissociation energetics (the total energy and enthalpy changes, except for $Al_2H_6^-(C_s)$ → $AlH_2^-(C_{2v})$ + $AlH_4(C_s)$) are much lower than the VDEs of the anions, which may reduce the experimental signals of the photodetached electrons. Furthermore, two anionic isomers may be formed by the structural rearrangement after the electron attachment or the efficient recombination between the neutral and anionic fragments.

The dialane anion is extremely interesting, owing to the novel electron-deficient 3c−2e and 2c−1e bonds. Although no infrared spectra of these two anions were reported in the matrix experiments,[2] they are valuable in future studies. In contrast to the traditional covalent (electron-pair) bonds described by Lewis's theory, odd-electron[18] and multiple (involved with the one-electron bonds)[19] bonds recently attracted much more interest. Here the 2c−1e bond playing an essential role in the stabilization[20] of the anion is reported for the first time.

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Supporting Information Available: Hybrids, occupancies, energies, and Cartesian coordinates and a scheme showing the transition between isomers. This information is available free of charge via the Internet at http:// pubs.acs.org.

References and Notes

(1) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.

(2) (a) Andrews, L.; Wang, X. *Science* **2003**, *299*, 2049. (b) Wang, X. Andrews, L.; Tam, S.; DeRose, M. E.; Fajardo, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 9218.

(3) For examples: (a) Duke, B. J.; Liang, C.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1991**, *113*, 2884. (b) Barone, V.; Orlandini, L.; Adamo, C. *J. Phys. Chem.* **1994**, *98*, 13185. (c) Magers, D. H.; Hood, R. B. Leszczynski, J. *Int. J. Quantum Chem. Symp.* **1994**, *28*, 579. (d) Shen, M.; Schaefer, H. *J. Chem. Phys.* **1992**, *96*, 2868.

(4) Ruščić, B.; Mayhew, C. A.; Berkowitz, J. *J. Chem. Phys.* **1988**, *88*, 5580.

(5) (a) Hara, M.; Domen, K.; Onishi, T.; Nozoye, H. *J. Phys. Chem.* **1991**, *95*, 6. (b) Breisacher, P.; Siegel, B. *J. Am. Chem. Soc.* **1964**, *86*, 5053.

(6) Rao, B. K.; Jena, P.; Burkart, S.; Ganteför, G.; Seifert, G. *Phys. Rev. Lett.* **2001**, *86*, 692.

(7) (a) Pullumbi, P.; Bouteiller, Y.; Mancerton, L. *J. Chem. Phys.* **1994**, *101*, 3610. (b) Andrews, L.; Wang, X. *J. Phys. Chem. A* **2004**, *108*, 4202.

(8) Pluta, C.; Porschke, K. R.; Kruger, C.; Hildenbrand, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 388.

(9) (a) Göbl, M.; Bonifacic, M.; Asmus, K. D. *J. Am. Chem. Soc.* **1984**, *106*, 5984. (b) Chatgilialogu, C.; Amus, K.-D. *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Plenum Press: New York and London, 1990.

(10) (a) Ortiz, J. V. *J. Chem. Phys.* **1996**, *104*, 7599. (b) Ferreira, A. M.; Seabra, G.; Dolgounitcheva, O.; Zakrzewski, V. G.; Ortiz, J. V. In *Quantum-Mechanical Prediction of Thermochemical Data*; Cioslowski, J., Ed.; Kluwer: Dordrecht, The Netherlands, 2001; p 131.

(11) Frisch, M. J.; et al. *GAUSSIAN 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO Version 3.0*, University of Wisconsin: Madison, 1990.

(13) Schaftenaar, V. *MOLDEN*; CAOS/CAMM Center: The Netherlands, 1991.

(14) (a) Taylor, H. S. In *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; Interscience Publishers: New York, 1970; Vol. XVIII. (b) O'Malley, T. F. *Phys. Rev.* **1966**, *150*, 14.

(15) See Table 3S of the Supporting Information. The prediction of one imaginary frequency of the C_s symmetrical AlH_4 is artificial, because it is energetically more stable than the C_1 symmetric at all levels of theory.

(16) The second-perturbation energy, $E(2) = n_\sigma F_{ij}^2/\delta\epsilon$, where n_σ is the density of the occupied σ orbital, $\delta\epsilon$ is the energy difference between the σ and unoccupied σ^* orbitals, and F_{ij} is the Fock matrix element between the σ and σ^* orbitals. Theory can be found in: Reed, A.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. Results can be found in Table 4S of the Supporting Information.

(17) See Table 4S of the Supporting Information, and: Sauers, R. R. *Tetrahedron* **1999**, *55*, 10013.

(18) Braida, B.; Thogersen, L.; Wu, W.; Hiberty, P. C. *J. Am. Chem. Soc.* **2002**, *124*, 11781.

(19) Gagllardl, L.; Roos, B. O. *Nature* **2005**, *433*, 848.

(20) VDE of $Al_2H_6^-(D_{3d})$ of 3.23 eV is due to the single 2c−1e bond formation; thereby the electrostatic repulsive energy of the neutral at the anionic structure is estimated to be 1.41 eV, according to the dissociation energy −1.82 eV of $Al_2H_6^-(D_{3d})$ → $2AlH_3(D_{3h})$ + e^-.