chemical reference data where no correction has been made for the energy shift between the dye monomer in acetonitrile and on the surface of AgBr.

Acknowledgments. R.K. and F.W. are grateful to the Deutsche Forschungsgemeinschaft, SFB 337, for financial support. The authors thank Steven Wickes at Polaroid for the preparation of the AgBr emulsions and K. Schwarzburg, FHI, for development and execution of the second curve-fitting procedure applied in this work.

Striking Similarities between Elementary Silicon and Aluminum Compounds: Monobridged, Dibridged, Trans-Bent, and Vinylidene Isomers of Al_2H_2

Zoltán Palágyi,[†] Roger S. Grev,* and Henry F. Schaefer, III

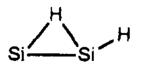
Contribution from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602. *Received April 3, 1992*

Abstract: Ab initio quantum mechanical methods have been used to study the singlet potential energy surface of Al_2H_2. Optimum geometries and harmonic vibrational frequencies were obtained for four geometrical isomers using the self-consistent-field (SCF), configuration interaction (CI), and coupled cluster (CC) methods. Both correlation methods including single and double excitations (CISD, CCSD) were employed, and all wave functions were determined with both DZP and TZ2P basis sets. Final energy predictions are obtained using large atomic natural orbital basis sets, and including the effects of triple excitations perturbatively using CCSD(T) methods. We found the planar dibridged structure to be the global minimum, as predicted earlier by Baird. However, our analysis also predicts the existence of a remarkable monobridged minimum, which has recently been observed experimentally for Si_2H_2. Two additional low-lying minima are found, corresponding to trans-bent and vinylidene-like structures. The dibridged, monobridged, and trans-bent structures can be understood as resulting from the three possible ways of coordinating the two electron-rich sites of diatomic AlH to the electron-deficient aluminum centers. The energy of these structures with respect to dissociation to two AlH monomers is quite low and is related to the large difference between the first and second Al-H bond dissociation energies of the parent AlH_3 compound.

Introduction

The development of techniques for the synthesis of naked aluminum clusters has increased the possibility of experimental investigations of aluminum hydrides.[1] Such compounds might serve as hydrogen storage devices or may be exploited as low-mass high-energy fuels. Previous theoretical studies[2] of Al_xH_y systems have revealed some of the peculiar characteristics of Al-H bonding, in particular, the role of hydrogen providing bridging bonds between aluminum atoms. Similar structures have been studied in boron,[3-6] aluminum-boron,[7] silicon,[8,9] germanium,[9,10] and gallium[11] hydrides.

The principal motivation for this research is a remarkable recent experimental discovery in the laboratory of Destombes.[12] Via microwave spectroscopy, the French group was able to observe the unconventional monobridged structure (1) of Si_2H_2 predicted 2 years earlier in theoretical studies.[8] In those studies, Colegrove[8] predicted 1 to be a genuine minimum on the Si_2H_2 potential energy hypersurface using a triple zeta plus double polarization (TZ2P) basis set in conjunction with the single and double excitation configuration interaction (CISD) method. At the highest level of theory (TZ2P + diffuse + f CISD + Davidson's correction), the unexpected monobridged structure 1 is second only in energy to the nonplanar dibridged ground state[8,13] of Si_2H_2. This result has been confirmed in more exhaustive theoretical studies of Si_2H_2.[14]



(1)

In molecules for which classically bonded alternatives exist (thus, excluding hydrogen bonds, for example), unsymmetrical monobridged structures are rare, and Si_2H_2 is the only one that has been experimentally observed to our knowledge. Such monobridged structures have, however, been found to be low-lying stable minima in theoretical studies of B_2H_4,[3] and Al_2H_4,[2b] and Ga_2H_4,[11] as well as in the heavier group 14 compounds Sn_2H_4 and Pb_2H_4.[9b] Therefore, one goal of the present research was to determine whether the Al_2H_2 system, with two fewer electrons than Si_2H_2, also possesses a low-lying unsymmetrical monobridged molecular structure. A previous study of Al_2H_2 by Baird[2a] optimized only planar trans-bent and doubly bridged singlet states, using the 3-21G* basis set at the SCF level of theory; whether the structures were minima or not was never explicitly stated. We now know that such low-level theoretical studies are incapable

---

[†] Permanent address: Quantum Theory Group, Physical Institute, Technical University, H-1521, Budapest, Hungary.

(1) See, for example: Hamrick, Y. M.; Van Zee, R. J.; Weltner, W. *J. Chem. Phys.* **1992,** *96,* 1767.

(2) (a) Baird, N. C. *Can. J. Chem.* **1985,** *63,* 71. (b) Lammertsma, K.; Guner, O. F.; Drewes, R. M.; Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1989,** *28,* 313. (c) McKee, M. L. *J. Phys. Chem.* **1991,** *95,* 6519.

(3) Mohr, R. A.; Lipscomb, W. N. *Inorg. Chem.* **1986,** *25,* 1053.

(4) Jouany, C.; Barthelat, J. C.; Daudey, J. P. *Chem. Phys. Lett.* **1987,** *136,* 52.

(5) (a) Sana, M.; Leroy, G.; Henriet, Ch. *J. Mol. Struct.* (*THEOCHEM*) **1989,** *187,* 233. (b) Sana, M.; Leroy, G.; Henriet, Ch. *J. Chim. Phys.* **1990,** *87,* 1.

(6) (a) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989,** *90,* 4314. (b) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989,** *91,* 4809. (c) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989,** *91,* 5118.

(7) Mains, G. J.; Bock, C. W.; Trachtman, M.; Finley, J.; McNamara, K.; Fisher, M.; Wociki, L. *J. Phys. Chem.* **1990,** *94,* 6996.

(8) Colegrove, B. T.; Schaefer, H. F. *J. Phys. Chem.* **1990,** *94,* 5593.

(9) (a) Trinquier, G. *J. Am. Chem. Soc.* **1990,** *112,* 2130. (b) Trinquier, G. *J. Am. Chem. Soc.* **1991,** *113,* 144.

(10) Grev, R. S.; DeLeeuw, B. J.; Schaefer, H. F. *Chem. Phys. Lett.* **1990,** *165,* 257.

(11) Lammertsma, K.; Leszczynski, J. *J. Phys. Chem.* **1990,** *94,* 5543.

(12) Cordonnier, M.; Bogey, M.; Demuynck, C.; Destombes, J.-L. *J. Chem. Phys.* **1992,** *97,* 7984.

(13) Bogey, M.; Bolvin, H.; Demuynck, C.; Destombes, J. L. *Phys. Rev. Lett.* **1991,** *66,* 413.

(14) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1992,** *97,* 7990.

0002-7863/93/1515-1936$04.00/0

Table I. Relative Energies (kcal/mol) of Stationary-Point Structures for the Al_2H_2 System (Only the Final Column Includes Zero-Point Vibrational Energies)

	SCF		CISD[a]		CCSD		CCSD(T)			
isomer	DZP	TZ2P	DZP	TZ2P	DZP	TZ2P	DZP	TZ2P[c]	ANO[c]	"best"
linear $^1\Delta$	32.5	29.2	40.9 43.0	37.6 39.9						40.2[e]
linear $^3\Sigma_g^-$	17.9	13.4	28.1 30.8	25.2 28.5						28.8[e]
trans	15.4	14.1	18.4 17.9	16.1 15.5	18.5	16.1	17.8	15.5	14.2	13.5[d]
mono-bridged	9.8	8.9	11.8 12.1	10.2 10.3	12.4	10.7	12.0	10.3	9.1	8.5[d]
branched	4.0	0.5	10.6 12.2	7.0 8.5	11.9	8.2	12.4	8.9	7.4	7.6[d]
planar[b] dibridged	0.0	0.0	0.0 0.0	0.0 0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a] The lower number in the CISD columns is the Davidson corrected energy difference. [b] Total energies (au) for the dibridged structure are as follows: DZP SCF, −484.913 638; TZ2P SCF, −484.945 919; DZP CISD, −485.050 317; DZP CISD+Q, −485.064 967; TZ2P CISD, −485.099 752; TZ2P CISD+Q, −485.118 378; DZP CCSD, −485.061 855; TZ2P CCSD, −485.114 617; DZP CCSD(T), −485.065 510; TZ2P CCSD(T), −485.119 663,[c] ANO CCSD(T), −485.142940.[c] [c] At the TZ2P CCSD optimized geometry. [d] ANO CCSD(T) including TZ2P CCSD harmonic zero-point vibrational energy correction. [e] TZ2P CISD+Q including TZ2P SCF harmonic zero-point vibrational energy correction.

of even qualitatively describing the Si_2H_2 potential energy surface; electron correlation must be explicitly included.[8] In this work, therefore, large basis sets and correlated methods are used to investigate the low-lying singlet-state minima of Al_2H_2.

Theoretical Methods

Several stationary points on the Al_2H_2 potential energy surface were initially located by using SCF gradient techniques[15,16] in conjunction with two different basis sets, designated DZP and TZ2P. The DZP basis consists of a standard Huzinaga–Dunning–Hay[17–19] double-ζ basis set of contracted Gaussian functions augmented by a set of six Cartesian d-like functions on aluminum ($\alpha_d(Al) = 0.40$) and a set of p-like functions on hydrogen ($\alpha_p(H) = 0.75$). The contraction scheme for this DZP basis is

$$Al(11s7p1d/6s4p1d),\ H(4s1p/2s1p)$$

The TZ2P basis set is a triple-ζ set in the valence shell and has two sets of polarization functions per atom. For hydrogen we used the standard Huzinaga–Dunning triple-ζ basis and polarization function orbital exponents of 1.5 and 0.375. For aluminum we used McLean and Chandler's[20] contraction of Huzinaga's 12s9p primitive Gaussian set augmented with two sets of six Cartesian d-like functions with orbital exponents of 0.8 and 0.2. The contraction scheme is thus

$$Al(12s9p2d/6s5p2d),\ H(5s2p/3s2p)$$

We determined the SCF quadratic force constants and harmonic vibrational frequencies using analytic energy second-derivative methods.[21] The electronic structures of the closed-shell structures have been investigated with the aid of localized orbitals, obtained by the method of Pipek and Mezey.[22]

Starting with the SCF geometries and force constants, we then reoptimized the structures using the configuration interaction (CI) method[23] and then the coupled cluster (CC) method.[24] Only the valence electrons have been correlated explicitly; the core-like SCF molecular orbitals (Al 1s, 2s, 2p) and their virtual orbital counterparts were not included in the CI and CC procedures. Otherwise, all single and double excitations from the SCF reference wave function have been included (CISD, CCSD). The CISD energies have been corrected to include the effects of unlinked quadruple excitations using Davidson's formula.[25] These corrected energies are denoted CISD+Q. We obtained CISD and CCSD harmonic vibrational frequencies by taking finite differences of analytic energy gradients.[26,27]

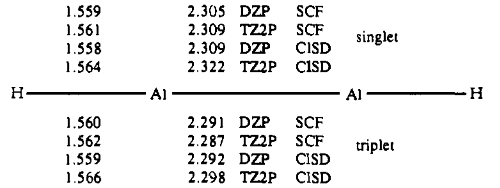


Figure 1. Theoretical stationary-point geometries for linear Al_2H_2 in its lowest singlet ($^1\Delta_g$) and triplet ($^3\Sigma_g^-$) electronic states. Bond distances are in Å.

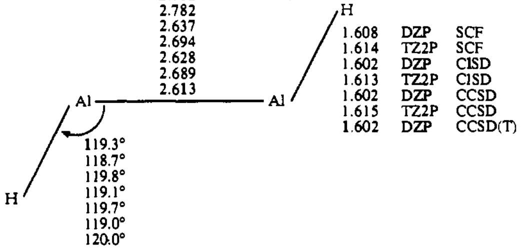


Figure 2. Theoretical geometries for the trans closed-shell singlet state of Al_2H_2. Bond distances are in Å.

Structures, Energies, and Bonding

In this section are presented results for the stationary-point geometries depicted in Figures 1–5. Three levels of theory (SCF, CISD, CCSD) have been used to obtain these structures, each with two basis sets (DZP, TZ2P). The relative energies as well as the total energies for the dibridged structure are given in Table I. Table II summarizes the predicted harmonic vibrational frequencies and infrared (IR) intensities. Table III contains a list of the largest CI coefficients for each wave function and the corresponding electronic configurations. Finally, in Table IV we report the energetic stabilities with respect to two AlH molecules. In this discussion, only the results obtained with the TZ2P CCSD method will be reported explicitly, unless otherwise indicated. Standard Cotton coordinate systems have been used, and whenever there is a choice of coordinate systems the Al atoms have been chosen to lie along the *x* axis.

We begin our discussion with the linear Al_2H_2 structures (Figure 1). The $^3\Sigma_g^-$ state is found to lie 12.4 kcal mol^{-1} (TZ2P CISD)

---

(15) Pulay, P. *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 4, pp 53–183.

(16) Dupuis, M.; King, H. F. *J. Chem. Phys.* **1978**, *68*, 3998.

(17) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(18) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(19) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 3, pp 1–27.

(20) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(21) Saxe, P.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1982**, *77*, 5647.

(22) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.

(23) Saxe, P.; Fox, D. J.; Schaefer, H. F.; Handy, N. C. *J. Chem. Phys.* **1982**, *77*, 5584.

(24) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1988**, *89*, 7382.

(25) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

(26) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *85*, 1963.

(27) Scheiner, A. C.; Scuseria, G. E.; Rice, J. E.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 5361.

Table II. Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for Al_2H_2 Structures

isomer		description	DZP SCF	TZ2P SCF	DZP CISD	TZ2P CISD	DZP CCSD	TZ2P CCSD
trans	b_u	Al–H antisym stre	1889 (918)	1852 (1133)	1884 (713)	1825 (928)	1871 (660)	1806 (870)
	a_g	Al–H sym stre	1886 (0)	1847 (0)	1881 (0)	1821 (0)	1868 (0)	1802 (0)
	a_g	sym bend	515 (0)	511 (0)	532 (0)	512 (0)	532 (0)	510 (0)
	b_u	antisym bend	219 (131)	214 (152)	263 (51)	238 (63)	273 (36)	251 (45)
	a_g	Al-Al stre	161 (0)	185 (0)	258 (0)	239 (0)	267 (0)	246 (0)
	a_u	oop	229 (14)	226 (23)	212 (25)	217 (30)	199 (26)	208 (30)
monobridged	a'	terminal H–Al stre	1919 (565)	1898 (651)	1892 (480)	1848 (568)	1873 (450)	1822 (534)
	a'	bridging H sym stre	1275 (506)	1222 (460)	1302 (401)	1220 (375)	1299 (384)	1213 (363)
	a'	bridging H antisym stre	1029 (725)	974 (719)	1084 (527)	1012 (567)	1090 (484)	1016 (527)
	a'	H–Al–H bend	455 (31)	429 (41)	460 (16)	439 (18)	459 (14)	438 (15)
	a'	Al–Al stre	233 (40)	232 (40)	267 (32)	260 (31)	265 (30)	256 (29)
	a''	terminal H oop bend	277 (35)	265 (39)	174 (31)	200 (32)	126 (29)	173 (29)
branched	b_2	Al–H antisym stre	1944 (261)	1906 (373)	1933 (223)	1875 (329)	1920 (211)	1857 (316)
	a_1	Al–H sym stre	1945 (403)	1910 (497)	1925 (334)	1873 (424)	1911 (316)	1854 (404)
	a_1	H–Al–Al sym bend	847 (605)	847 (573)	833 (507)	814 (503)	827 (484)	804 (482)
	b_1	oop bend	431 (196)	442 (211)	377 (156)	405 (170)	359 (143)	395 (159)
	a_1	Al–Al stre	257 (32)	289 (33)	268 (27)	288 (31)	266 (25)	286 (29)
	b_2	H–Al–H in-plane wag	262 (46)	277 (54)	239 (37)	253 (46)	235 (35)	250 (44)
planar dibridged	a_g	sym Al–H stre	1475 (0)	1439 (0)	1474 (0)	1399 (0)	1474 (0)	1386 (0)
	b_{3u}	H's → same Al	1313 (3103)	1254 (3124)	1371 (2458)	1279 (2470)	1376 (2352)	1277 (2371)
	b_{1g}	H's → opposite Al's	1035 (0)	1015 (0)	1168 (0)	1097 (0)	1178 (0)	1094 (0)
	b_{2u}	antisym Al–H stre	1020 (141)	1006 (123)	1061 (126)	1001 (119)	1065 (125)	995 (119)
	a_g	Al–Al stre	326 (0)	329 (0)	333 (0)	329 (0)	333 (0)	327 (0)
	b_{1u}	oop bend	322 (163)	298 (188)	200 (172)	236 (159)	167 (164)	227 (145)

isomer		description	DZP SCF singlet	TZ2P SCF singlet	DZP SCF triplet	TZ2P SCF triplet
linear	σ_g	Al–H sym stre	2088 (0)	2071 (0)	2086 (0)	2065 (0)
	σ_u	Al–H antisym stre	2075 (255)	2059 (258)	2073 (256)	2052 (283)
	σ_g	Al–Al stre	522 (0)	518 (0)	530 (0)	531 (0)
	π_u	cis bend	419 (91)	423 (70)	420 (92)	425 (73)
	π_g	trans bend	320i (0)	274i (0)	453i (0)	334i (0)

below the $^1\Delta_g$ state. Because of the double bond between the aluminum atoms, the Al–Al bond distance is by far the shortest for the linear structures, and so are the Al–H bond distances. These results are reflected in the high values for the stretching vibrational frequencies. While the $^3\Sigma_g^-$ state is the ground state for B_2H_2, for Al_2H_2 the linear structure lies energetically highest above the planar dibridged ground state and is also unstable with respect to splitting into two AlH molecules at the levels of theory considered. Both the triplet and the singlet linear states have a doubly degenerate (π_g) imaginary vibrational frequency corresponding to two equivalent trans bending motions. The reversal of the stability of the linear and dibridged structures in B_2H_2, compared to Al_2H_2 and the instability of the linear structure toward trans-bending in Al_2H_2 are exactly analogous to the trends seen in C_2H_2 versus Si_2H_2.[8]

The lower energy of the trans structure (Figure 2) compared to the linear $^1\Delta_g$ state can be considered to be an example of the second-order Jahn–Teller stabilization.[28] Upon trans bending, the doubly degenerate π_u orbital splits into b_u and a_u orbitals

---

(28) (a) Bader, R. F. W. *Can. J. Chem.* **1962,** *40,* 1164. (b) Pearson, R. G. *J. Am. Chem. Soc.* **1969,** *91,* 4947. (c) Pearson, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1975,** *72,* 2104. (d) Cherry, W.; Epiotis, N.; Borden, W. T. *Acc. Chem. Res.* **1977**, *10,* 167.

Table III. Coefficients Greater Than 0.05 in the TZ2P CISD Wave Functions for the Different Al_2H_2 Structures

isomer	coefficient	configuration
linear singlet	0.945	$(core)4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^2$
	−0.072	$2\pi_u^2 \rightarrow 2\pi_g^2$
	−0.066	$4\sigma_g \rightarrow 9\sigma_g$
	−0.057	$5\sigma_g \rightarrow 9\sigma_g$
linear triplet	0.949	$(core)4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^2$
trans	0.933	$(core)5a_g^2 5b_u^2 6a_g^2 6b_u^2$
	−0.137	$6b_u^2 \rightarrow 7a_g^2$
	−0.050	$6b_u^2 \rightarrow 7a_g 10a_g$
monobridged	0.938	$(core)9a'^2 10a'^2 11a'^2 12a'^2$
	−0.071	$12a'^2 \rightarrow 13a'^2$
branched	0.941	$(core)7a_1^2 8a_1^2 3b_2^2 9a_1^2$
planar dibridged	0.938	$(core)4a_g^2 2b_{2u}^2 4b_{3u}^2 5a_g^2$
	−0.075	$5a_g 4b_{3u} \rightarrow 2b_{2g} 2b_{u1}$
	−0.062	$5a_g 4b_{3u} \rightarrow 2b_{1g} 4b_{2u}$

corresponding to in-plane and out-of-plane π bonds, respectively. The in-plane π bond component is stabilized on bending by mixing with the low-lying σ_u orbital of the linear structure, which is also of b_u symmetry in the C_{2h} subgroup of $D_{\infty h}$. Further stabilization is provided by the mixing of occupied σ_g and low-lying unoccupied π_g orbitals of linear Al_2H_2 upon trans-bending. The small energy gap between these two trans MO's makes the trans triplet state 13.9 kcal mol^{-1} lower than the singlet at the DZP SCF level. However, by including electron correlation, the singlet state becomes more stable by 5.1 kcal mol^{-1} (DZP CISD). Our TZ2P TCSCF wave functions, which correlate with the $^1\Delta_g$ state at linearity, show that the coefficient of the $5a_g^2 5b_u^2 6a_g^2 2a_u^2$ configuration gradually decreases with trans bending to a value of 0.120 at equilibrium, leaving the dominant $5a_g^2 5b_u^2 6a_g^2 6b_u^2$ SCF configuration and resulting in higher in-plane electron density. The small value of the coefficient for the second configuration at the optimized trans-bent geometry justifies the subsequent use of single configuration based methods for this structure.

The Al-Al bond distance in the closed-shell trans geometry, 2.689 Å, is nearly 0.4 Å longer than that obtained for the linear structure. This structure is, by far, the most affected by basis set and electron correlation. At the SCF level of theory, the DZP and TZ2P basis sets yield identical Al-Al distances. After accounting for correlation effects at the CCSD level of theory, the TZ2P bond distance is 0.06 Å longer than that obtained with the DZP basis set, but both basis sets give considerably shorter Al-Al distances at correlated levels of theory than they do with SCF methods. For all the closed-shell structures investigated here, the geometrical changes upon introduction of electron correlation are larger with DZP than with TZ2P basis sets. This often happens in weakly bound systems, such as hydrogen-bonded or datively bonded structures, and can generally be attributed to basis set superposition errors (BSSE), which are enhanced at correlated levels of theory. With the larger TZ2P basis set, BSSE is reduced, and the structural changes are more regular. A dative bond description is indeed appropriate for the trans-bent structure, as the localized bond analysis clearly reveals a pair of highly distorted banana-type bonds between the aluminum atoms; i.e., the structure is effectively that of two weakly interacting Al-H fragments, with each Al-H fragment donating its lone pair of electrons into the empty *p*-orbital of the other. Similar models have been used to describe the bonding in trans-bent, nominally double-bonded Ge_2H_4, Sn_2H_4, and Pb_2H_4.[29]

A common feature of the molecular structures corresponding to minima on the potential surface is a small HOMO-LUMO gap and a low-lying LUMO. We have studied the lowest triplet states for the branched, bridged, and dibridged isomers as well, and found them to be higher lying than the corresponding singlet states already at the SCF level. Thus for these structures we investigated only the singlet electronic states with the higher levels of theory.

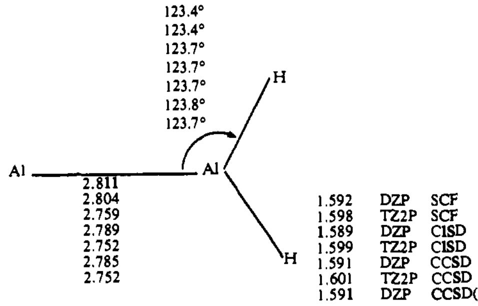


Figure 3. Theoretical geometries for the vinylidene-like closed-shell singlet state of Al_2H_2. Bond distances are in Å.

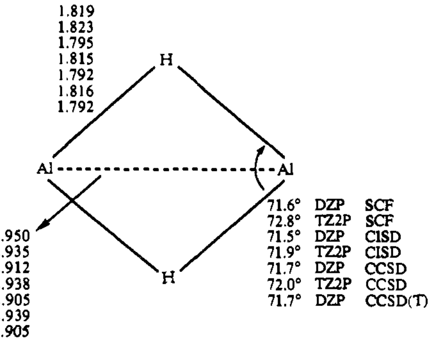


Figure 4. Theoretical equilibrium geometries for the closed-shell singlet, planar dibridged electronic ground state of Al_2H_2. Bond distances are in Å.

The branched or vinylidene-like structure (Figure 3) is planar, and the molecule has C_{2v} symmetry. Of the four closed-shell structures investigated here, this is the only one that invites a classical bonding description, i.e., involving exclusively two-center, two-electron bonds. Thus, the localized bond analysis reveals a pair of Al-H σ bonds, the two aluminum atoms are joined by a σ bond, and the terminal aluminum atom has a lone pair of electrons. The Al-Al bond distance, 2.785 Å, is nearly 0.1 Å longer than that in the trans structure. This structure is a genuine potential minimum and it lies 8.2 kcal mol^{-1} above the dibridged global minimum. The vibrational frequency corresponding to the out-of-plane bend is quite high (395 cm^{-1}) compared to the other isomers.

The planar dibridged isomer (Figure 4) is the global minimum for Al_2H_2. This isomer has D_{2h} symmetry, with the hydrogens in bridging positions between the aluminum atoms. The localized bond analysis shows that there is a lone pair on each aluminum, and the remaining four valence electrons occupy two symmetric three-center (Al-H-Al) bridging bonds. Thus, this structure can be considered as a dimer of AlH in which the negatively charged hydrogen atoms are acting as the electron donors to the acidic aluminum centers. This is in contrast with the trans-bent structure where the aluminums are the donors. The Al-Al cage distance and Al-H bridge are 0.32 Å and 0.09 Å longer than the corresponding "typical" experimental values ($Me_2AlH_2AlMe_2$).[2c,30] The lowest vibrational frequency for this isomer is the out-of-plane bending of the hydrogens preserving C_{2v} symmetry. We have not found a stationary point corresponding to this "butterfly" structure, which is, of course, the global minimum for the Si_2H_2 molecule.[8,13,14]

Thus far, we have seen two modes of coordinating two AlH monomers: (1) using the lone pairs of aluminum to datively bond

---

(29) (a) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261. (b) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387. (c) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 3871. (d) Trinquier, G.; Malrieu, J.-P.; Riviere, P. *J. Am. Chem. Soc.* **1982**, *104*, 4529. (e) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303. (f) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 5916. (g) Trinquier, G.; Malrieu, J.-P. *J. Phys. Chem.* **1990**, *94*, 6184.

(30) Baxter, P. L.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1986**, 805.

Table IV. Energies of Al_2H_2 Structures Relative to 2(AlH) (kcal/mol). Only the Final Column Includes Zero-Point Vibrational Energies (ZPVE)

	SCF		CISD[a]		CCSD		CCSD(T)			
isomer	DZP	TZ2P	DZP	TZ2P	DZP	TZ2P	DZP	TZ2P[c]	ANO[c]	"best"
linear $^1\Delta$	12.2	9.2	13.2 14.3	10.8 12.3						15.2[e]
linear $^3\Sigma_g^-$	−2.4	−6.6	0.4 2.1	−1.6 0.9						3.8[e]
trans	−4.9	−5.9	−9.3 −10.8	−10.7 −12.1	−9.5	−10.6	−11.5	−12.9	−15.8	−13.7[d]
monobridged	−10.5	−11.1	−15.9 −16.6	−16.6 −17.3	−15.6	−16.0	−17.3	−18.1	−20.9	−18.7[d]
branched	−16.3	−19.5	−17.1 −16.5	−19.8 −19.1	−16.1	−18.5	−16.9	−19.5	−22.6	−19.6[d]
planar dibridged	−20.3	−20.0	−27.7 −28.7	−26.8 −27.6	−28.0	−26.7	−29.3	−28.4	−30.0	−27.2[d]
2(AlH)[b]	0.0	0.0	0.0 0.0	0.0 0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a] The lower number in the CISD columns is the Davidson corrected energy difference. [b] The "supermolecule" method was used to obtain the total CISD energies for AlH. [c] At the TZ2P CCSD optimized geometry. [d] ANO CCSD(T) including TZ2P CCSD harmonic zero-point vibrational energy correction. [e] TZ2P CISD+Q including TZ2P SCF harmonic zero-point vibrational energy correction.

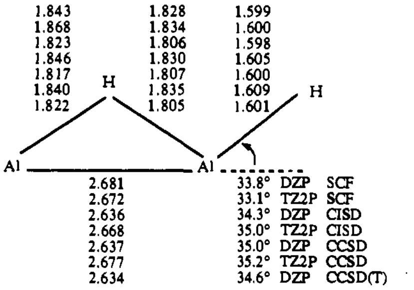


Figure 5. Theoretical geometries for the monobridged closed-shell singlet state of Al_2H_2. Bond distances are in Å.

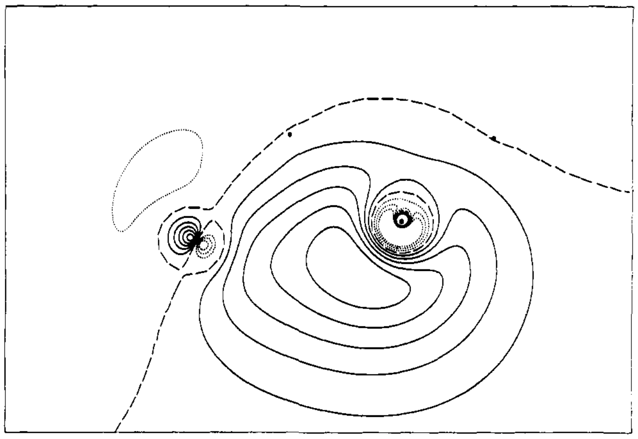


Figure 6. An aluminum lone pair, deformed by the p component from the terminal aluminum atom. In this figure the values of the TZ2P SCF localized orbital for the monobridged isomer of Al_2H_2 are plotted in the plane of the molecule. Nuclei are arranged as in Figure 5 and noted by heavy dots. Solid, dashed, and dotted lines correspond to positive, zero, and negative values of the function. The step between two adjacent contour lines is 0.025.

to the electron-deficient sites on the other aluminum, resulting in the trans-bent isomer (Figure 2), and (2) using the negatively charged hydrogens as the donors to the acidic sites of aluminum, resulting in the planar dibridged isomer (Figure 3). What about the third alternative, where one of the donors is the aluminum lone pair, and the other is the negatively charged hydrogen? The monobridged isomer (Figure 5) fits this description exactly! It is a genuine minimum lying 10.7 kcal mol^{-1} above the planar dibridged and 2.5 kcal mol^{-1} above the branched (vinylidene-like) isomer at the TZ2P CCSD level of theory. Analysis of the localized bonds shows an aluminum lone pair being donated from the aluminum connected to the terminal hydrogen to the other aluminum (Figure 6), as well as a three-center, two-electron bond through the bridging hydrogen (Figure 7). In addition, the terminal hydrogen is connected to one of the aluminum atoms by a conventional σ bond (Figure 8) and there is a lone pair on the other aluminum (Figure 9). The resulting Al–Al bond lengths (2.634 Å) is intermediate between the values for a single and a double bond, and slightly (0.06 Å) shorther than that for the trans isomer.

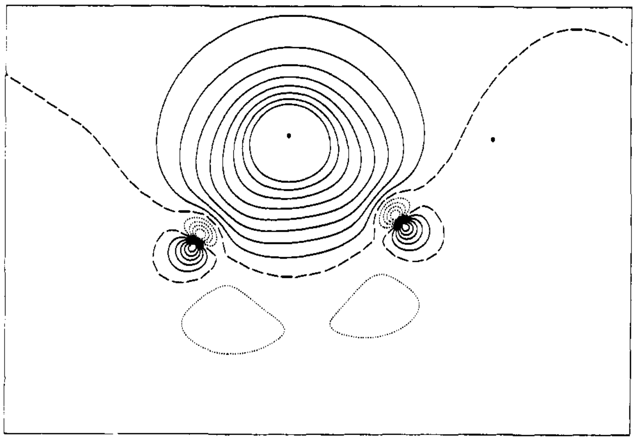


Figure 7. Three-center two-electron bond involving the two aluminum atoms and the bridging hydrogen. For interpretation, see caption for Figure 6.

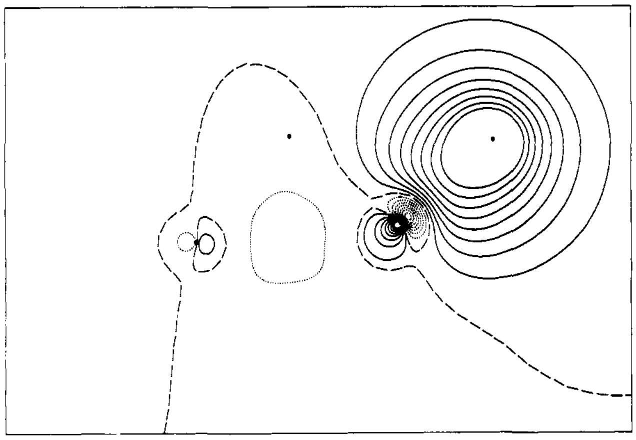


Figure 8. The conventional single bond connecting the terminal hydrogen atom to one of the aluminum atoms. For interpretation, see caption for Figure 6.

Although we have not attempted to locate any transition states, by analogy with Si_2H_2[8,14] the monobridged structure is most likely obtained from the branched (vinylidene-like) structure by following

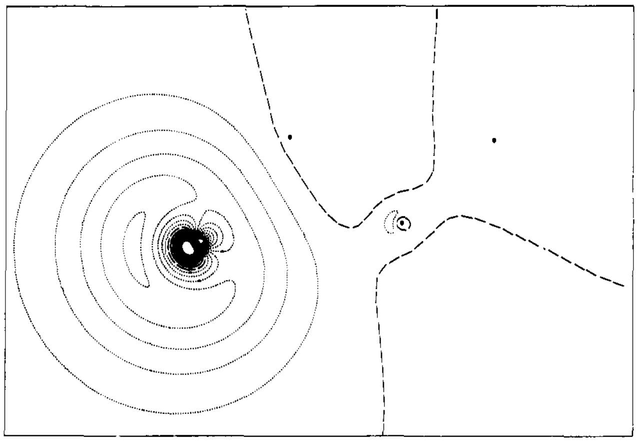


Figure 9. Lone pair on the terminal aluminum atom. For interpretation, see caption for Figure 6.

the in-plane wag motion of the latter, which has a vibrational frequency of 250 cm^{-1}. Similarly, the out-of-plane bending frequency in the monobridged isomer is quite low (173 cm^{-1}) and presumably leads to the transition state for rearrangement to the planar dibridged minimum. The rearrangement barriers are probably small, but this does not preclude the observation of monobridged Al_2H_2; in Si_2H_2, for which the monobridged isomer has been observed and characterized,[12] the barrier is predicted to be 3.7 kcal mol^{-1}[14] A more fundamental stumbling block to the observation of the monobridged isomer is its small dipole moment, 0.26 D. The vinylidene-like isomer has a much larger dipole moment, 1.55 D. This trend is the opposite of that in Si_2H_2,[14] where the monobridged isomer has a larger dipole moment than the vinylidene isomer. This partially explains the inability to observe the vinylidene isomer of Si_2H_2 in microwave studies.[12] Our results suggest that microwave detection of the vinylidene isomer of Al_2H_2 is advantageous.

In light of the near degeneracy of the low-lying unsymmetrical monobridged (Figure 3) and vinylidene-like (Figure 4) structures of Al_2H_2, it was decided to press on to yet a higher level of theory. For this purpose the CCSD(T) method, proposed in 1989 by Raghavachari et al.,[31] was used in conjunction with Scuseria's analytic gradient procedure.[32] In this manner DZP CCSD(T) stationary-point geometries were optimized for the four closed-shell singlet structures of Al_2H_2. These additional structures have been included in Figures 2–5. We find that the DZP CCSD(T) structures differ imperceptibly from those optimized at the DZP CCSD level of theory, except for the trans-bent structure for which the Al–Al bond distance decreases by 0.015 Å. This breeds confidence in simply adopting the TZ2P CCSD optimized geometries for any further analysis. The DZP CCSD(T) stationary-point total energies show that the unsymmetrical monobridged structure falls 0.4 kcal mol^{-1} below the vinylidene-like structure of Al_2H_2. This is roughly the pattern of behavior predicted for Si_2H_2 by Colegrove.[8]

The order of the monobridged and vinylidene structures of Al_2H_2 could be reversed again if larger basis sets are used. Table I indicates that correlated energies of both structures decrease (relative to the planar dibridged global minimum) in going from the DZP to the TZ2P basis set. To investigate this further, we have determined single-point TZ2P CCSD(T) energies at the TZ2P CCSD optimized geometries. Additional single-point CCSD(T) energies, again at the TZ2P CCSD optimized geometries, are determined using the atomic natural orbital (ANO) basis sets of Widmark, Roos, et al.[33] Specifically, we have used the 5s4p3d2f ANO set for aluminum and the 3s2p1d ANO set for hydrogen.[33] Our final prediction, using the ANO CCSD(T) energies and correcting for differential zero-point vibrational effects at the TZ2P CCSD level of theory, is that the monobridged isomer lies 0.9 kcal mol^{-1} above the vinylidene-like isomer, and that both of these are within 9 kcal mol^{-1} of the dibridged ground-state structure.

Discussion

Trinquier[9] has extensively analyzed bridge-bonded structures in the group 14 compounds C_2H_4, Si_2H_4, Ge_2H_4, Sn_2H_4, and Pb_2H_4. Considered as dimers of MH_2, these molecules are very similar to Al_2H_2, because the monomers MH_2 for group 14 have similar donor and acceptor sites to those in AlH. For C_2H_4, bridged structures apparently do not exist as minima on the potential energy surface. Already at Si_2H_4, Trinquier finds that dibridged isomers emerge as low-lying stable minima, and they persist down the periodic table, becoming the ground states for Sn_2H_4 and Pb_2H_4. The third mode of coordination, with one donor being the lone pair and one being the bridging hydrogen (and the structure being monobridged), does not appear until we reach Sn_2H_4.[9] Removing two hydrogens from these systems yields stable minima that are associated with this unsymmetrical coordination mode already at the second row, with Si_2H_2, and now in Al_2H_2 as well.

The resemblance of the Al_2H_2 potential energy surface to that of Si_2H_2 is stunning! Each of the four singlet isomers of Al_2H_2 studied here has an exact analogue in Si_2H_2 that can be derived simply by adding two electrons to an unoccupied bonding π orbital in Al_2H_2. The only qualitative structural change in doing this is that the lowest lying dibridged isomer of Si_2H_2 is now nonplanar, instead of planar as in Al_2H_2. The planar dibridged isomer of Si_2H_2 is higher lying and is the transition state for degenerate inversion of the C_{2v} symmetry ground-state dibridged structure.[8,14] In addition, the energies of the monobridged, vinylidene, and trans-bent structures relative to the dibridged minimum are very similar in both case: +9, +12, and +16 kcal mol^{-1}, respectively, for Si_2H_2 [14], and +9, +8, and +14 kcal mol^{-1}, respectively, for Al_2H_2.

There *is* one significant difference between the Al_2H_2 and Si_2H_2 potential energy surfaces: Si_2H_2 is bound by 80–85 kcal mol^{-1} relative to two SiH molecules,[14,34] while Al_2H_2 is bound by only 27.2 kcal mol^{-1} relative to two AlH fragments at our highest level of theory (Table IV). The relative dissociation energies are reasonable, because Si_2H_2 has the extra pair of bonding electrons. What *is* remarkable is the small dissociation energy for Al_2H_2, when a naive interpretation would suggest that there are four electrons available for Al–Al bonding. The dissociation energy of ground-state B_2H_2, by contrast, is nearly 100 kcal mol^{-1}[5,6] Noting that the bonding in the lowest-lying dibridged isomer is dative in nature (or three-center, two-electron bonding) is hardly satisfying, because the dissociation energy in the alane dimer (Al_2H_6) is around 32 kcal mol^{-1},[35] which is larger than that found for Al_2H_2. Furthermore, the dissociation energy of the ground state of Al_2H_4 (which is of $HAl(\mu H_3)Al$ form; electronically, this is a salt-like $Al^+[AlH_4]^-$ species, with the Al^+ form coordinated to a face of AlH_4^-) into AlH_3 and AlH is near 36 kcal mol^{-1}[2b] Why, with all these additional free electron pairs, does a more stable isomer not result? The answer clearly lies in the stability of AlH itself.

Questions similar to this have been asked in group 14 chemistry, where it is found that the dissociation energies of the doubly bonded molecules disilene, $H_2Si{=}SiH_2$, digermene, $H_2Ge{=}GeH_2$, and germasilene, $H_2Ge{=}SiH_2$, are all found to be lower than those in the parent singly bonded isomers disilane, $H_3Si{-}SiH_3$, digermane, $H_3Ge{-}GeH_3$, and germasilane, $H_3Ge{-}SiH_3$, respectively. We have demonstrated[36] that the dissociation energies of the

---

(31) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(32) Scuseria, G. E. *J. Chem. Phys.* **1991**, *94*, 442.

(33) (a) Widmark, P.-O.; Malmqvist, P.-A.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291. (b) Widmark, P.-O.; Persson, J.; Roos, B. O. *Theor. Chim. Acta* **1991**, *79*, 419.

(34) (a) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1991**, *95*, 2416. (b) Curtiss, L. A.; Raghavachari, K.; Deutsch, P. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *95*, 2433. (c) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1990**, *94*, 5120.

(35) Rendell, A. P.; Lee, T. J.; Komornicki, A. *Chem. Phys. Lett.* **1991**, *178*, 462.

doubly bonded isomers are rigorously related to differences between first and second M–H bond dissociation energies (BDEs) in the parent hydrides, MH_4, as well as to standard M–M′ σ- and π-bond energies. Specifically, for the double-bond dissociation process

$$H_2M{=}M'H_2 \rightarrow MH_2 + M'H_2$$

the dissociation energy, $D(H_2M{=}M'H_2)$, is equal to

$$D(H_2M{=}M'H_2) = D(H_3M{-}M'H_3) + D_\pi - DSSE(MH_2) - DSSE(M'H_2) + [D(H_3M{-}H) - D(H_3M'MH_2{-}H)] + [D(H_3M'{-}H) - D(H_3MM'H_2{-}H)] \quad (2)$$

where DSSE(MH_2), the *divalent state stabilization energy*,[37] is the difference between the first and second bond dissociation energy in MH_4. That is, the DSSE is given by

$$DSSE(MH_2) = D(H_3M{-}H) - D(H_2M{-}H)$$

The two terms in brackets in eq (2) are the difference between the first M–H dissociation energies of the parent hydrides and the substituted hydrides, and these differences are usually small. Thus, to a good approximation, the double-bond dissociation energy is given by

$$D(H_2M{=}M'H_2) \approx D(H_3M{-}M'H_3) + D_\pi(M{=}M') - DSSE(MH_2) - DSSE(M'H_2) \quad (3)$$

We should note that eq 2 is correct only if the the π-bond energy, D_π, is determined by the method of Benson;[38] i.e., if D_π is given by

$$D_\pi(M{=}M') = \Delta H_f(H_3MM'H_2) + \Delta H_f(H_3M'MH_2) - \Delta H_f(H_3MM'H_3) - \Delta H_f(H_2M{=}M'H_2)$$

On the other hand, alternative definitions of π-bond energies exist, and one in particular, that of Schleyer and Kost,[39] is formulated in such a way that eq 3, and not eq 2, is correct. That is, Schleyer and Kost's definition of the π-bond energy is equal to Benson's π-bond energy, plus the bracketed terms in eq 2.

To make a long story[36] short, the reason that disilene, digermene, and germasilene have smaller double-bond dissociation energies than the single-bond dissociation energies in the parent saturated compounds is that SiH_2 and GeH_2 have large (≈20 kcal mol^{-1}), positive DSSEs, in conjuction, of course, with relatively small single-bond (≈70 kcal mol^{-1}) and π- bond (≈25 kcal mol^{-1}) energies. Equation 1 also provides a ready explanation of why the dissociation energy in ethylene is ≈20 kcal mol^{-1} *larger* than the sum of standard σ- and π-bond energies (because the DSSE of CH_2 is *negative*) and why that of tetrafluoroethylene is so small (because the DSSE of CF_2 is large and *positive*[36]).

The relevance of this digression to the current question of the dissociation energy of Al_2H_2 to 2AlH is this: the difference between the first and second Al–H BDEs in AlH_3 is nearly 40 kcal mol^{-1}! A modified eq 2 appropriate for group 13 compounds can be trivially obtained by eliminating one of the hydrogens bonded to each heavy atom, although the DSSE nomenclature then seems odd because AlH is *not* divalent. Nonetheless, the resulting equation would be appropriate for the trans-bent structure, which is our nearest candidate to a classical double-bonded structure. If we then use any reasonable values for standard Al–Al σ- and π-bond energies, the overall dissociation energy will come out to be near zero because we must subtract off two times 40, or 80 kcal mol^{-1}, for twice the difference in first and second bond dissociation energies in AlH_3. Preliminary studies suggest that the difference between the first and second BDEs in GaH_3 are about the same as those in AlH_3, so similar chemistry can be anticipated for Ga_2H_2.

Another consequence of DSSEs being large and positive in group 14 chemistry is that divalent isomers such as $H_3MM'H$ become low lying relative to the double-bonded isomer $H_2M{=}M'H_2$ when M′ = Si, Ge, or the heavier elements.[36,40] In this case, the former isomer is above the latter by the amount

$$D_\pi - DSSE(H_3MM'H) + D(H_3MM'H_2{-}H) - D(H_3M'MH_2{-}H)$$

For symmetrical systems (M = M′), this reduces to D_π − DSSE(H_3MMH). Applied to the current case of Al_2H_2, this becomes D_π − DSSE(H_2AlAl), and DSSE(H_2AlAl) will surely be large and positive, just as it is for AlH. Thus, the branched isomer H_2AlAl (Figure 4) is expected to be low lying, and indeed it is. By comparison, the H_2BB isomer lies 50 kcal mol^{-1} above the linear triplet HBBH ground state.[5] Note that BH also has a substantial difference in first and second B–H BDEs, around 28 kcal mol^{-1},[5,6] but the π-bond energy is clearly quite strong, as it is in all first-row compounds.

A different model, proposed by Carter and Goddard,[41] has been used in recent years to rationalize small double-bond dissociation energies. These authors assume that, for substituted ethylenes, the double-bond dissociation energies will be equal to that in ethylene unless one of the carbene fragments is a ground-state singlet, in which case the dissociation energy will be lowered (relative to that in ethylene) by the singlet–triplet splitting of the ground-state singlet carbene(s). This model has spawned a wave of singlet–triplet splitting rationalizations for interesting phenomena.[29e–g,42,43] Because both the singlet–triplet splitting model and the thermochemical analysis presented above, eq 2, are predicting the same qualitative behavior, it is tempting to equate the DSSE with the singlet–triplet splitting,[40,43] but in practice this fails.[40] In quantitative studies of double-bond dissociation energies, the singlet–triplet splitting model yields errors that are substantial, random, and of uncertain origin.[40,42,44] Furthermore, the singlet–triplet splitting model is *qualitatively* wrong if the substituents stabilize the triplet carbenes.[36] The crux of the matter is that it is the *stability* of the carbene fragments, not the singlet–triplet splitting, that is important.

Concluding Remarks

The singlet potential energy surface of Al_2H_2 has been analyzed extensively at the SCF, CISD, CCSD, and CCSD(T) levels of theory. Our results show the necessity of including correlation effects to accurately describe relative energies as well as the shape of the potential surface. The planar dibridged global minimum and the low-lying monobridged minimum demonstrate the importance of bridging hydrogen atoms in creating Al–Al bonds. The only classically bonded structure that emerges is the vinylidene-like structure. The other stable isomers are best viewed as AlH dimers with dative or three-center two-electron bonds derived from the three possible ways that the two electron-rich regions in the AlH monomer can donate electron density to the electron-deficient aluminum centers.

Each of the four stable singlet isomers of Al_2H_2 can be mapped, one-to-one, onto an analogous isomer of Si_2H_2 by the addition of a pair of bonding π electrons. The similarities between the stable minima of Al_2H_2 and Si_2H_2 extend to their relative energies, with isomeric energy differences varying by only a few kcal mol^{-1}. The analogy ends, however, when we consider their stability toward fragmentation, and we have tied this difference to the tremendous stability of the AlH monomer, as measured by the difference

---

(36) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125.

(37) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(38) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 63.

(39) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

(40) Grev, R. S.; Schaefer, H. F.; Baines, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 9458.

(41) (a) Carter, E. A.; Goddard, W. A. *J. Phys. Chem.* **1986**, *90*, 998. (b) Carter, E. A.; Goddard, W. A. *J. Chem. Phys.* **1988**, *88*, 1752. (c) Carter, E. A.; Goddard, W. A. *J. Chem. Phys.* **1988**, *88*, 3132. (d) Carter, E. A.; Goddard, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 4077.

(42) Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8589.

(43) Clauberg, H.; Minsek, D. W.; Chen. P. *J. Am. Chem. Soc.* **1992**, *114*, 99.

(44) Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 5573.

between first and second Al-H BDEs in the parent compound, AlH_3.

The presence of the unsymmetrical monobridged structure of Al_2H_2 as a genuine minimum proves that this structural type is not limited to Si_2H_2,[8,14] for which solid experimental structural confirmation now exists.[12] This work surely suggests that related potential energy hypersurfaces—B_2H_2, $BAlH_2$, $BGaH_2$, $AlGaH_2$, Ga_2H_2, $SiCH_2$, Ge_2H_2, $GeCH_2$, $GeSiH_2$—should be carefully searched for new unsymmetrical monobridged structures.

Acknowledgment. We thank Seung-Joon Kim, Yukio Yamaguchi, and Yaoming Xie for many helpful discussions. This research was supported by the U.S. Air Force Office of Scientific Research, Grant AFOSR-92-J-0047.

$PO_3^-\cdot(H_2O)_n$ Clusters. Molecular Anion Structures, Energetics, and Vibrational Frequencies

Buyong Ma, Yaoming Xie, Mingzuo Shen, and Henry F. Schaefer, III*

Contribution from the Center for Computational Quantum Chemistry, The University of Georgia, Athens, Georgia 30602. *Received July 20, 1992*

Abstract: The $PO_3^-\cdot(H_2O)_n$ clusters (n = 1, 2, and 3) have been studied using ab initio quantum mechanical methods. Self-consistent field (SCF), configuration interaction with single and double excitations (CISD), and coupled cluster single and double excitation (CCSD) levels of theory were employed in conjunction with basis sets of quality double-zeta (DZ), double-zeta plus polarization (DZP), and DZP plus diffuse functions. The most important finding is that the clusters prefer to form high-symmetry double donor–double acceptor hydrogen bonds between the PO_3^- anion and the H_2O molecules. The hydrogen bond lengths increase and the dissociation energies decrease with the addition of successive water molecules. The hydrogen bond in $PO_3^-\cdot H_2O$ has a dissociation energy (D_0 = 13.3 kcal mol^{-1}) about 0.5 kcal mol^{-1} less than that for $NO_3^-\cdot H_2O$. The D_{3h} $PO_3^-\cdot(H_2O)_3$ theoretical results do not agree with the experimental thermochemistry concerning the nature of the hydration of $PO_3^-\cdot(H_2O)_2$ by the third water molecule. The latter finding is consistent with the conclusions of Keesee and Castleman.

1. Introduction

Beginning with the experiments of Henchman, Viggiano, Paulson, Freedman, and Wormhoadt,[1] the metaphosphate anion, PO_3^-, has been shown to be relatively stable and unreactive in the gas phase.[2] However, there is strong laboratory evidence that the PO_3^- anion does not exist as a free entity in aqueous solution,[3] unlike its nitrogen congener NO_3^-. This fact, together with the well-known role of PO_3^- in biological systems[4] and interesting features associated with its bonding and electronic structure,[5] has given impetus to several theoretical and experimental studies. Very recently, experiments have established that PO_3^- is a weaker base than I^- and that PO_3^- is one of the least reactive bases to have been characterized thermodynamically.[6] Therefore, it is important to understand the unusual behavior of PO_3^- in the gaseous phase. The key reactions with water are[2]

$$PO_3^- + (H_2O)_n \rightarrow PO_3^-\cdot(H_2O)_n$$

$$PO_3^-\cdot(H_2O)_n + H_2O \rightarrow H_2PO_4^-\cdot(H_2O)_n$$

The intermediate clusters $PO_3^-\cdot(H_2O)_n$ are very important to the understanding of the properties of PO_3^- in both the gaseous and solution phases. Experimentally it has been shown[1] that the $PO_3^-\cdot(H_2O)_n$ clusters are stable in the gaseous phase and that the isomerization barrier varies with the number of water molecules, n. Unfortunately, there is no theoretical research concerning the $PO_3^-\cdot(H_2O)_n$ clusters. Although there is considerable laboratory thermochemical data from the important work of Keesee and Castleman,[2] there is very little experimental structural information concerning PO_3^- and its clusters. In fact, since $PO_3^-\cdot(H_2O)_{n+1}$ and $H_2PO_4^-\cdot(H_2O)_n$ are indistinguishable by mass spectrometry, there may be some uncertainty about the nature of the observed clustering as well as the isomerization behavior of PO_3^-.

Since the hydrogen bonding in the $NO_3^-\cdot H_2O$ system has been investigated previously,[7,8] the current study attempts to make meaningful comparisons between the hydration behaviors of PO_3^- and NO_3^-. This paper will consider the structures and properties of the $PO_3^-\cdot(H_2O)_n$ clusters, for n = 0, 1, 2, and 3. Such a theoretical investigation was explicitly called for in the 1989 laboratory study of Keesee and Castleman.[2]

2. Theoretical Methods

The basis sets adopted here include STO-3G (minimum basis set),[9] double-zeta (DZ),[10,11] double-zeta plus polarization (DZP),[12] and DZP plus diffuse functions (DZP+diff) for the P and O atoms. The basis set denoted DZP for hydrogen is the (4s/2s) set[8] with the set of p functions having orbital exponents $\alpha_p(H)$ = 0.75; for the oxygen and phosphorus atoms we chose the Huzinaga–Dunning–Hay bases[10-12] O(9s5p/4s2p),

---

(1) Henchman, M.; Viggiano, A. A.; Paulson, J. F.; Freedman, A.; Wormhoadt, J. *J. Am. Chem. Soc.* **1985**, *107*, 1453.

(2) Keesee, R. G.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 9015.

(3) (a) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161. (b) Ramirez, F.; Marecek, J.; Minore, J.; Srivastava, S.; leNoble, W. *J. Am. Chem. Soc.* **1986**, *108*, 348. (c) Burgess, J.; Blundell, N.; Cullis, P. M.; Hubbard, C. D.; Misra, R. *J. Am. Chem. Soc.* **1988**, *110*, 7900. (d) Freeman, S.; Friedman, J. M.; Knowles, D. *J. Am. Chem. Soc.* **1987**, *109*, 3166. (e) Cullis, P. M.; Nicholls, D. *J. Chem. Soc., Chem. Commun.* **1987**, 783.

(4) Westheimer, F. H. *Chem. Rev.* **1981**, *81*, 313. Westheimer, F. H. *Science* **1987**, *235*, 1173. Related systems of biological significance have been the subject of many theoretical studies, for example: Pullman, A.; Berthod, H.; Gresh, N. *Chem. Phys. Lett.* **1975**, *33*, 11.

(5) Rajca, A.; Rice, J. E.; Streitwieser, A., Jr.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 4189.

(6) Viggiano, A. A.; Henchman, M. J.; Dale, F.; Deakyne, C. A.; Paulson, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 4299.

(7) Shen, M.; Xie, Y.; Schaefer, H. F.; Deakyne, C. A. *J. Chem. Phys.* **1990**, *93*, 3379.

(8) Shen, M.; Xie, Y.; Schaefer, H. F.; Deakyne, C. A. *Chem. Phys.* **1991**, *151*, 187.

(9) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2659.

(10) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(11) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

0002-7863/93/1515-1943$04.00/0