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Aluminirene (HAlC₂H₂) and Aluminirane (HAlC₂H₄): Aluminum-Substituted Counterparts of Cyclopropene and Cyclopropane

Yaoming Xie and Henry F. Schaefer III*

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Abstract: The theoretical molecular structures, energetics, and vibrational frequencies of isomers of HAl–acetylene and HAl–ethylene have been predicted by ab initio quantum mechanical methods. Standard double-ζ plus polarization (DZ+P) basis sets, triple-ζ plus polarization (TZ+P), and triple-ζ plus double polarization (TZ+2P) basis sets have been used for full geometry optimizations in conjunction with self-consistent-field (SCF) and single and double excitation configuration interaction (CISD) methods. The predictions are in good agreement among the different theoretical methods. The TZ+P CISD dissociation energies of AlC_2H_3 with respect to $AlH + C_2H_2$ were found to be 27.7 kcal/mol for the aluminirene ring structure, while $H_2AlC=CH$ and :$AlCH=CH_2$ are more stable by 14.4 and 19.8 kcal/mol, respectively. Similarly the dissociation of AlC_2H_5 to $AlH + C_2H_4$ is endothermic by 6.9 kcal/mol for the aluminirane ring structure, while $H_2AlCH=CH_2$ and :$AlCH_2CH_3$ are more stable by 21.4 and 26.1 kcal/mol, respectively. It is clear that the global minima of these simple Al–hydrocarbon systems do not correspond to three-membered rings but rather to monovalent aluminum bonding situations in conjunction with normal CH and CC bonds. Harmonic vibrational frequencies and infrared intensities are predicted for all systems with DZ+P, TZ+P, and TZ+2P SCF methods. All vibrational frequencies of the six structures are real, demonstrating that they are minima on their potential energy hypersurfaces. Finally, for the more frequently studied radical system AlC_2H_4, this work presents the first theoretical investigation of the ethylene insertion product $HAlCH=CH_2$, which turns out to be the global minimum for AlC_2H_4.

Introduction

The study of aluminum–hydrocarbon compounds is becoming an active area within organometallic chemistry. A range of adducts, such as $AlCH_4$,[1] AlC_2H_2,[2-4] AlC_2H_4,[3-7] and $Al(C_2H_4)_2$,[8] have been observed by ESR, IR, or UV spectroscopies. In the meantime, theoretical studies of AlC_2H_2[9,10,12] and AlC_2H_4[9,11] have

also made some significant progress and allowed improved interpretations of the experiments. These aluminum complexes are open-shell radicals, which, as suggested in ref 12, are expected to form more stable corresponding closed-shell compounds by simply adding one electron to the singly occupied molecular orbital, although no experimental results have been reported to date. The hydrogenated Al–C_2H_2 and hydrogenated Al–C_2H_4 systems are representative of this hypothetical class of compounds. It is of interest to predict answers to the following questions: Should these corresponding closed-shell compounds exist? If so, which are the

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Table I. Geometries and Energies of Aluminirene (Structure 1, Figure 1) and Comparison with the Three-Membered-Ring Isomer of the Al-C$_2$H$_2$ Radical (Results in Parentheses Are from SCF Theory, and Those Appearing First Are from CISD Theory)

	H-Al-C$_2$H$_2$ aluminirene (C_{2v})			Al-C$_2$H$_2$ ($^2A_1$) 3-membered ring
	TZ+2P	TZ+P	DZ+P	DZ+P^a
Al—H, Å	1.557 (1.558)	1.551 (1.556)	1.552 (1.556)	
Al—C, Å	1.852 (1.842)	1.851 (1.845)	1.851 (1.844)	1.866 (1.855)
C=C, Å	1.370 (1.362)	1.371 (1.362)	1.384 (1.371)	1.383 (1.368)
C=H, Å	1.079 (1.076)	1.084 (1.079)	1.089 (1.082)	1.089 (1.082)
C—C—H, deg	126.9 (126.8)	127.3 (127.2)	126.9 (126.8)	127.0 (127.0)
E, hartree	-319.66400 (-319.32632)	-319.64102 (-319.31878)	-319.62424 (-319.31493)	-319.00008 (-319.70995)
E(Davidson), hartree	-319.70410	-319.67767	-319.65949	-319.03244
ΔE,^{b} kcal·mol^{-1}	29.2 (24.1)	27.7 (22.0)	32.8 (26.6)	
ΔE(Davidson),^{b} kcal·mol^{-1} 28.2	28.2	27.1	32.2	

^{a} Earlier theoretical predictions.[12] ^{b} $\Delta E = E(\text{AlH} + \text{C}_2\text{H}_2) - E(\text{aluminirene})$.

more stable structures? What are the dissociation energies of these species? And furthermore, what should the infrared spectra of these species look like? The present paper attempts to provide the answers for the hydrogenated Al–C$_2$H$_2$ and hydrogenated Al–C$_2$H$_4$ systems by the means of ab initio quantum mechanical methodology. The predictions may assist in the identification of such new compounds in future experimental studies. In the present paper, we present the studies of six distinct molecular structures, of which three are isomers of HAlC$_2$H$_2$ while the other three are isomers of HAlC$_2$H$_4$.

Theoretical Approach

The smaller basis set used in this research was of double-ζ plus polarization (DZ+P) quality. Specifically the atomic contracted Gaussian basis set may be designated Al(11s7p1d/6s4p1d),[13,14] C(9s5p1d/4s2p1d),[15,16] H(4s1p/2s1p).[15,16] Chosen polarization function orbital exponents were α_d(Al) = 0.4, α_d(C) = 0.75, and α_p(H) = 0.75. The scale factor for the hydrogen primitive Gaussian s functions was $(1.2)^2 = 1.44$.

Stationary point geometries were fully optimized with both self-consistent-field (SCF) and configuration interaction (CI) analytic gradient methods[17,18] with the DZ+P basis set. The CI wave functions included all Hartree-Fock-interacting single and double excitations (CISD) with respect to the single-configuration SCF wave function. The molecular systems studied here are all reasonably well described by single-configuration SCF theory. Among the molecular structures considered 3 (see below) has the smallest value of C_0, the coefficient of the SCF configuration in the CISD wave function. This value $C_0 = 0.9386$ implies that the SCF configuration is 88.1% of the CISD wave function. Thus the CISD wave functions should yield reliable predictions.

In order to investigate further the effects of basis set, we also used larger basis sets of triple-ζ plus polarization (TZ+P) and triple-ζ plus double polarization (TZ+2P) quality, designated Al(11s7p1d/7s5p1d), C(9s5p1d/5s3p1d), H(4s1p/3s1p), and Al(11s7p2d/7s5p2d), C(9s5p2d/5s3p2d), H(4s2p/3s2p). The TZ basis set differs from DZ only in the more flexible contraction of the Huzinaga primitive sets, which are inherently of valence double-ζ quality; thus the term TZ here does not mean that there are three distinct basis functions for each valence atomic orbital. The single polarization function orbital exponents were the same as those for DZ+P, and the double polarization function orbital exponents were chosen as α_d(Al) = 0.2, 0.8, α_d(C) = 0.375, 1.50, and α_p(H) = 0.375, 1.50, which were based on a rule suggested by Pople et al.[19] The hydrogen s functions were also scaled by $(1.2)^2 = 1.44$. With the TZ+P basis set, geometries of all the systems in this paper were also optimized at both SCF and CISD

levels. However, with the larger TZ+2P basis set, all were optimized at the SCF level, but only two structures were optimized at the CISD level.

Harmonic vibrational frequencies were evaluated with the analytic second derivative method at all of the DZ+P, TZ+P, and TZ+2P SCF levels of theory.

Aluminirene

In our previous theoretical study,[12] there was identified a low-lying isomer ($^2A_1$) of the ·Al–C$_2$H$_2$ complex with three-membered-ring structure
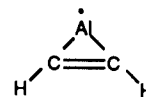

Its electron configuration (with core molecular orbitals $1a_1^2 2a_1^2 1b_2^2 3a_1^2 2b_2^2 1b_1^2 4a_1^2$ included implicitly) is

$$5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 4b_2^2 8a_1$$
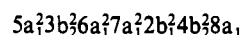
This structure incorporates two conventional aluminum–carbon single bonds and a carbon–carbon double bond. The half-occupied molecular orbital (8a$_1$) is located on the aluminum atom, and one electron may be simply added on this molecular orbital to a closed-shell anion. Protonation of this $\bar{\text{A}}$lC$_2$H$_2$ species at the aluminum yields the aluminirene molecule.

Aluminirene

1
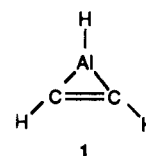
is accordingly a compound with the closed-shell electron configuration

$$5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 4b_2^2 8a_1^2$$
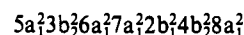
In the CISD wave function for aluminirene the seven core-like SCF MOs (1s, 2s, 2p Al and 1s C) are constrained to be doubly occupied in all configurations. Similarly, at the DZ+P level, the seven highest virtual orbitals (core counterparts) are deleted from the CI procedure. In this way, there are 17 162 configurations with the DZ+P basis set. However, at the TZ+P and TZ+2P CISD levels, only the three highest virtual orbitals (i.e. 1s core counterparts) are deleted since the core counterparts of the 2s and 2p Al orbitals may not have the highest virtual orbital energies. Thus there are 33 115 configurations with the TZ+P basis set and 62 752 configurations with the TZ+2P basis set in C_{2v} symmetry. Table I and Figure 1 show the equilibrium geometries with DZ+P, TZ+P, and TZ+2P basis sets at both SCF and CISD levels of theory. Comparisons of its energy and geometry with the $^2A_1$ ·Al–C$_2$H$_2$ radical as well as the dissociation energies with respect to the separated AlH plus C$_2$H$_2$ are also shown in the same table.

The total energy of aluminirene (1) at the DZ+P SCF level is -319.31493 hartrees, which is 26.6 kcal/mol lower than infinitely separated AlH (-242.44063 hartrees) and C$_2$H$_2$ (-76.83190

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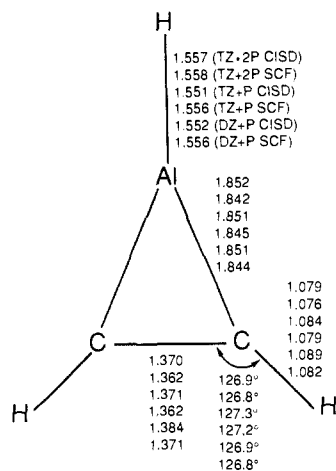(19) Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1984**, *80*, 3265.

Al-Substituted Counterparts of c-C₃H₆ and c-C₃H₄

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H

| 1.557 (TZ+2P CISD) |
| 1.558 (TZ+2P SCF) |
| 1.551 (TZ+P CISD) |
| 1.556 (TZ+P SCF) |
| 1.552 (DZ+P CISD) |
| 1.556 (DZ+P SCF) |

Al
1.852
1.842
1.851
1.845
1.851
1.844

1.079
1.076
1.084
1.079
1.089
1.082

C ——————— C

1.370
1.362   126.9°
1.371   126.8°
1.362   127.3°
1.384   127.2°
1.371   126.9°
         126.8°

H

H

Figure 1. Ab initio equilibrium geometries for the aluminirene (structure 1) molecule. All bond distances are in angstroms.

hartrees). At the DZ+P CISD level, the total energy of the supermolecular system of (100 bohr) separated AlH and C_2H_2 is -319.571 90 hartrees, so that this dissociation energy increases to 32.8 kcal/mol. It becomes 32.2 kcal/mol [(-319.608 22) - (-319.659 49) hartrees] if Davidson's correction[20] is included. For the larger TZ+P basis set, the dissociation energy is 22.0 kcal/mol at SCF level and 27.7 kcal/mol at the CISD level (27.1 kcal/mol if Davidson's correction is included). For the TZ+2P basis set, the three values of dissociation energies are 24.1, 29.2, and 28.2 kcal/mol. The results show that aluminirene is an energetically lower lying system than the separated AlH plus C_2H_2, with a significant dissociation energy (about 30 kcal/mol). In other words, aluminirene might be expected to be prepared at least from an energetic viewpoint.

As seen in Table I and Figure 1, the theoretical results for the geometrical parameters of aluminirene are in good agreement among different theoretical levels, with respect to either the size of the basis sets or the effect of the electron correlation. The differences among theoretical methods are very small. The range of change of bond lengths is about 0.01 Å or less, and that of bond angles is less than 0.5°. An interesting observation is that Al-H bond lengths, in contrast to many other chemical bonds, become longer when the basis set is extended and become shorter when electron correlation is taken into account. The same phenomenon, that correlation effects shortened the Al-H bond lengths (and Al-C bond length in some cases), was also noticed for most conformations of the ·Al-C₂H₂ and ·Al-C₂H₄ radical systems.[11,12] The Al-H bond length is predicted as 1.551-1.558 Å, which is not sensitive to the level of theory. The Al-H bond length, 1.557 Å at the TZ+2P CISD level, which is the highest level we used, is very close to the normal experimental Al-H bond length in $H_3AlN(CH_3)_3$, 1.560 Å.[22] The predicted Al-C bond length in aluminirene at the TZ+2P CISD level is 1.852 Å, which is 0.105 Å shorter than for the experimentally characterized[21] trimethylaluminum, for which r(Al-C) = 1.957 Å. The predicted C=C double bond length is 1.370 Å, which is 0.03 Å longer than the standard value.

Table I also shows that the change in geometrical parameters is very small from the ²A₁ radical to aluminirene, although only the DZ+P basis set results are available for this comparison. There is no change (to within 0.001 Å) for the C-H bond length, and only a 0.001 Å increase in the C=C bond length with the CISD method (or 0.003 Å with SCF). The difference in the C-C-H angle is also very small: 0.2° for SCF, and 0.1° for CISD. But the Al-C bond in aluminirene becomes shorter than that for

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Table II. Theoretical Harmonic Vibrational Frequencies (cm⁻¹) for Aluminirene (Structure **1**, Figure 1) at the SCF Level and Comparison with the ²A₁ State of the Three-Membered-Ring Al-C₂H₂ with Infrared Intensities (km/mol) Given in Parentheses

sym	description	TZ+2P SCF	TZ+P SCF	DZ+P SCF	²A₁ Al-C₂H₂ DZ+P SCF[a]
a₁	C-H stretch	3307 (19)	3300 (19)	3327 (25)	3326 (28)
b₁	C-H stretch	3289 (17)	3281 (17)	3308 (20)	3306 (18)
a₁	Al-H stretch	2085 (124)	2097 (145)	2096 (152)	
a₁	C-C stretch	1484 (0.2)	1494 (0.1)	1498 (0.2)	1496 (0.4)
b₁	C-H bend	1309 (14)	1302 (17)	1298 (16)	1258 (25)
a₂	C-H wag	1132 (0)	1113 (0)	1100 (0)	1097 (0)
a₁	C-H bend	1035 (<0.1)	1034 (0.3)	1028 (0.7)	1016 (1)
a₁	Al-C stretch	817 (52)	817 (54)	823 (56)	809 (62)
b₁	Al-C stretch	732 (39)	733 (32)	734 (32)	713 (53)
b₂	C-H wag	729 (175)	725 (219)	716 (219)	706 (145)
b₁	Al-H bend	546 (89)	545 (108)	547 (110)	
b₂	Al-H wag	491 (90)	493 (93)	495 (93)	

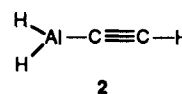[a] Earlier theoretical predictions.[12]

the ²A₁ ·AlC₂H₂ radical (0.011 Å shorter at the SCF level and 0.015 Å at the CISD level), because of the change from an unpaired electron to the Al-H bond. All things considered, the model of aluminirene as the conjunction of a hydrogen atom with the ²A₁ Al-C₂H₂ radical is a good one.

Harmonic vibrational frequencies and IR intensities at the DZ+P, TZ+P, and TZ+2P SCF levels are given in Table II. All 12 frequencies for aluminirene are real, of which the smallest one is nearly 500 cm⁻¹. This suggests that aluminirene is a stable minimum on its potential energy hypersurface. The effect of the size of basis set is small. The changes from DZ+P to TZ+2P are about 1% or less except for the a₂ C-H wag mode (32 cm⁻¹ or about 3%) and the b₂ Al-H wag mode (13 cm⁻¹ or about 2%). Comparing with the ²A₁ radical at the DZ+P level, the changes of fundamental frequencies and intensities are small. There are only a few wavenumber differences for the C-C and C-H stretching modes, consistent with the unchanged bond lengths. The frequencies for the two Al-C stretch modes (a₁ and b₁) are upshifted by 21 and 14 cm⁻¹, respectively, from those for the ²A₁ radical, which is consistent with the 0.011-Å shortened Al-C bond distance. The large change of frequency for the b₁ C-H bend mode is unexpected; it might be caused by the change of Al-C-H angle.

Like the ²A₁ radical, the strongest infrared band of this closed-shell compound arises from the C-H wag mode. At the TZ+2P SCF level this fundamental is located at 729 cm⁻¹ with 175 km/mol IR intensity, while it is predicted at 725 cm⁻¹ with 219 km/mol using the TZ+P basis set and at 716 cm⁻¹ with 219 km/mol using the DZ+P basis set. In addition, there are three other strong fundamentals related to the Al-H bond, which is not present for the ²A₁ ·Al-C₂H₂ radical. They correspond to the stretching, bending, and wagging motions of the Al-H bond. At the TZ+2P SCF level, these frequencies at 2085, 546, and 491 cm⁻¹, with IR intensities 124, 89, and 90 km/mol, respectively. (The DZ+P and TZ+P basis sets give very close results.) It was pointed out[12] that the two Al-C stretching frequencies with reasonable intensities might serve as a signature for the three-membered-ring isomer of the Al-C₂H₂ radical. For aluminirene, they are 817 and 732 cm⁻¹ with considerable intensities of 52 and 39 km/mol at the TZ+2P SCF level. The three intense bands associated with the Al-H stretch, bend, and wag modes might also be helpful in the identification of the closed-shell molecule aluminirene.
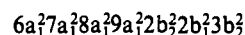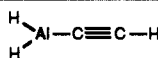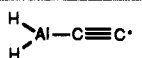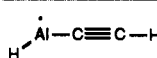
Ethynylalane

Another plausible isomer of AlC₂H₃ is ethynylalane (C_{2v})

H
  ⟩Al—C≡C—H
H

2

with electron configuration

$6a_1^2 7a_1^2 8a_1^2 9a_1^2 2b_2^2 2b_1^2 3b_1^2 3b_2^2$

Table III. Geometries and Energies of Ethynylalane (Structure 2, Figure 2) and Comparison with Two Related Radicals (Results in Parentheses Are at the SCF Level, and Those Appearing First Are at the CISD Level of Theory)

	H\\Al—C≡C—H / H /			H\\Al—C≡C· / H /	·Al—C≡C—H / H /
	TZ+2P	TZ+P	DZ+P	DZ+P	DZ+P^a
Al—H, Å	1.566 (1.569)	1.562 (1.568)	1.562 (1.568)	1.560 (1.566)	1.574 (1.578)
Al—C, Å	1.916 (1.918)	1.912 (1.919)	1.913 (1.918)	1.916 (1.921)	1.919 (1.924)
C≡C, Å	1.206 (1.192)	1.210 (1.195)	1.223 (1.203)	1.230 (1.205)	1.225 (1.204)
C—H, Å	1.059 (1.055)	1.061 (1.057)	1.069 (1.062)		1.069 (1.062)
C—Al—H, deg	119.0 (119.0)	119.2 (119.1)	119.2 (119.1)	118.7 (118.7)	117.9 (117.8)
E, hartree	−319.68575	−319.66396	−319.64267	−318.93887	−319.01108
	(319.35209)	(−319.34757)	(−319.33933)	(−318.65691)	(−318.72834)
E(Davidson), hartree	−319.72593	−319.70006	−319.67746	−318.97272	−319.04232
ΔE,^{b} kcal·mol^{-1}	42.8 (40.3)	42.1 (40.0)	44.4 (41.9)		
ΔE(Davidson),^{b} kcal·mol^{-1}	41.8	41.1	43.4		

^{a} Earlier theoretical predictions.[12] ^{b} ΔE = E(AlH + C_2H_2) − E(ethynylalane).
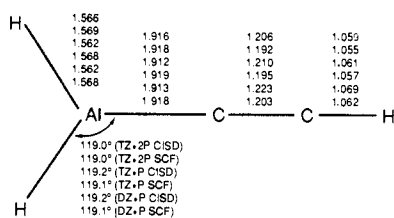
Figure 2. Ab initio equilibrium geometries for the ethynylalane (structure 2) molecule. All bond distances are in angstroms.

The DZ+P CISD wave functions for this electronic state include a total of 17 550 configurations keeping seven core MOs doubly occupied and deleting seven counterpart virtual MOs. The TZ+P CISD wave functions include 33 817 configurations, and the TZ+2P CISD includes 63 865, for which only three virtual orbitals were deleted. Ethynylalane may be regarded as the conjunction of either the H atom with the C—H insertion product radical HÁl—C≡C—H (C_s) or the H atom with the $^2A_1$ RC_2 radical H_2Al—C≡C· (C_{2v}). Table III and Figure 2 show the structural parameters of ethynylalane (2), and Table III also shows the comparison of energies and geometries with its two "parent" radicals. The total energy of ethynylalane (2) at DZ+P SCF is −319.339 33 hartrees, which is 41.9 kcal/mol lower than this infinitely separated AlH and C_2H_2 system. At the DZ+P CISD level, it is lower by 44.4 kcal/mol than the supermolecular system with 100-bohr separation between AlH and C_2H_2. This dissociation energy changes to 43.4 kcal/mol when Davidson's correction[20] is included. When the basis set is enlarged to TZ+P and TZ+2P, the dissociation energies at the SCF level change only slightly, i.e. to 40.0 and 40.3 kcal/mol, respectively. It increases to 42.1 kcal/mol at the TZ+P CISD level (to 41.1 kcal/mol when including Davidson's correction) and to 42.8 kcal/mol at the TZ+2P CISD level (to 41.8 kcal/mol with Davidson's correction). Relative to aluminirene (1), the energy of ethynylalane (2) is lower by 15.3 kcal/mol at the DZP SCF level and 11.6 kcal/mol at the DZP CISD level (18.0 and 14.4 kcal/mol for TZ+P SCF and CISD; 16.2 and 13.6 kcal/mol for TZ+2P SCF and (CISD). This suggests that ethynylalane is a preferable structure to aluminirene (1) if the other factors, like activation energies, are not major considerations.

The predicted geometrical parameters for ethynylalane are also not strongly dependent on basis set and correlation effects. The changes in Al—H and Al—C bond lengths are not larger than 0.007 Å. The Al—C bond length, 1.916 Å (TZ+2P CISD), is closer to the normal value (1.957 Å, in trimethylaluminum) than structure 1. However, like the Al—H bond length in structure 1, the Al—H bond lengths in structure 2 become longer as the basis set is extended and become shorter as the correlation energy is taken into account. Correlation effects also reduce the Al—C bond length. Comparing 2 with its two "parent" radicals (DZP results), all bond lengths for ethynylalane are very similar (0.006 Å or less), except for the Al—H bond in HÁl—C≡C—H. This change is probably due to the influence of the new adjacent Al—H bond. We can also

Table IV. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) for Ethynylalane (Structure 2, Figure 2) at the SCF Level with Infrared Intensities (km/mol) Given in Parentheses

| sym	description	TZ+2P SCF	TZ+P SCF	DZ+P SCF
a_1	C—H stretch	3593 (34)	3603 (34)	3618 (35)
a_1	C—C stretch	2262 (69)	2266 (69)	2257 (70)
a_1	Al—H stretch	2045 (107)	2054 (115)	2055 (119)
b_1	Al—H stretch	2042 (217)	2051 (239)	2052 (247)
a_1	AlH$_2$ scissors	849 (376)	858 (430)	859 (433)
b_2	C—H wag	843 (48)	881 (42)	851 (50)
b_1	C—H bend	804 (50)	841 (46)	807 (53)
b_2	AlH$_2$ wag	664 (340)	673 (393)	673 (393)
a_1	Al—C stretch	597 (65)	601 (67)	606 (66)
b_1	AlH$_2$ rock	595 (143)	603 (158)	604 (156)
b_1	Al—C—C bend	215 (4)	225 (6)	228 (5)
b_2	Al—C—C wag	199 (6)	218 (8)	228 (7)

compare the geometrical parameters of ethynylalane with those of acetylene at the same theoretical levels. The change in C–H bond length is very small (<0.002 Å for DZ+P, TZ+P, and TZ+2P basis sets with both SCF and CISD methods), but the C≡C bond in ethynylalane, which falls under the influence of the adjacent Al atom, is 0.12–0.14 Å longer.

Harmonic vibrational frequencies and IR intensities of ethynylalane, at the DZ+P SCF, TZ+P SCF, and TZ+2P SCF levels of theory, are shown in Table IV. Although, as expected, most of the frequencies decrease when the size of the basis set increases, the changes in the frequencies and intensities are quite small. Most of the differences for the frequencies are less than 10 cm^{-1} or relatively speaking 1%. The exceptions are the Al–C–C bend and wag modes at the TZ+2P SCF level (215 cm^{-1}), which are 10–20 cm^{-1} too small, and the Al–H wag and bend modes at the TZ+P level (881 and 841 cm^{-1}), which are almost 40 cm^{-1} too large. The latter is really surprising, but we notice the same behavior for the π_u and π_g C–H bend frequencies of isolated acetylene (877 and 820 cm^{-1}) which are about 20–40 cm^{-1} larger at the TZ+P SCF level than at the DZ+P or TZ+2P levels. There are quite a few intense IR fundamentals for ethynylalane, most of which are correlated with the two Al–H bonds. At the TZ+2P SCF level, the strongest band is at 849 cm^{-1} with 376-km/mol IR intensity, namely the a_1 AlH$_2$ scissors mode. The second strongest IR fundamental is the b_2 AlH$_2$ wag at 664 cm^{-1} (340 km/mol). Three other vibrations with IR intensities >100 km/mol are the b_1 AlH$_2$ rock at 595 cm^{-1} (143 km/mol) and the two Al–H stretches (a_1 and b_1) at 2045 cm^{-1} (107 km/mol) and 2042 cm^{-1} (217 km/mol). These strong IR bands may serve as signatures for the H$_2$Al-group. The predicted C≡C stretching vibration is predicted (TZ+2P SCF) at 2262 cm^{-1} with intensity 69 km/mol. (As a comparison, the harmonic C≡C stretching frequency of acetylene at the TZ+2P SCF level is 2211 cm^{-1}, but it is IR forbidden.) Also of significant intensity are the a_1 Al–C stretch at 597 cm^{-1} (65 km/mol), the b_1 C–H bend at 804 cm^{-1} (50 km/mol), and the a_1 C–H stretch at 3593 cm^{-1} (34 km/mol). It is hoped that these IR features can be used for the laboratory identification of ethynylalane.

Al-Substituted Counterparts of c-C₃H₆ and c-C₃H₄

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Table V. Geometries and Energies of Vinylaline (Structure 3, Figure 3, Which Gives the Connectivity of the Distinct C and H Atoms) and Comparison with the Trans σ-Bonded Al–C₂H₂ Complex (Results in Parentheses Are at the SCF Level, and Those Appearing First Are at the CISD Level of Theory)

	TZ+2P	TZ+P	DZ+P	DZ+Pᵃ
Al–C, Å	(1.989)	1.989 (1.994)	1.984 (1.989)	1.993 (1.997)
C–C, Å	(1.329)	1.341 (1.331)	1.353 (1.340)	1.323 (1.316)
C–H, Å	(1.081)	1.089 (1.085)	1.093 (1.087)	1.090 (1.087)
C–H, Å	(1.080)	1.088 (1.083)	1.092 (1.085)	1.091 (1.081)
C–H, Å	(1.077)	1.085 (1.080)	1.089 (1.082)	
C–C–Al, deg	(115.9)	116.6 (118.8)	116.2 (118.3)	107.2 (115.9)
C–C–H, deg	(116.1)	115.3 (115.6)	114.9 (115.3)	119.9 (117.0)
C–C–H, deg	(122.0)	121.9 (122.1)	121.9 (122.1)	134.0 (134.4)
C–C–H, deg	(123.6)	124.0 (123.6)	123.7 (123.4)	
E, hartree	(−319.35831)	−319.67264 (−319.35381)	−319.65570 (−319.34971)	−318.99078 (−318.70619)
E(Davidson), hartree		−319.71044	−319.69214	−319.02539
ΔE,ᵇ kcal·mol⁻¹	(44.2)	47.5 (43.9)	52.6 (48.4)	
ΔE(Davidson),ᵇ kcal·mol⁻¹		47.7	52.7	

ᵃEarlier theoretical predictions.[12] ᵇΔE = E(AlH + C₂H₂) − E(vinylaline).
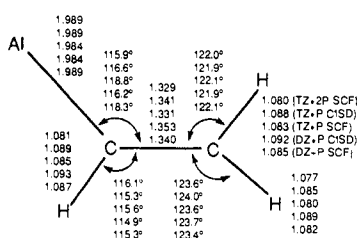

Figure 3. Ab initio equilibrium geometries for the vinylaline (structure 3) molecule. All bond distances are in angstroms.

Vinylaline

Another possible closed-shell isomer of AlC₂H₃ is vinylaline (C_s), in which there is a lone pair at the Al atom. We take the

3
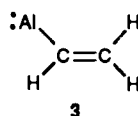
name *aline* to describe monovalent aluminum molecules of the general type :Al–R. The electron configuration of vinylaline is

$$7a'^{2}8a'^{2}9a'^{2}10a'^{2}11a'^{2}2a''^{2}12a'^{2}$$
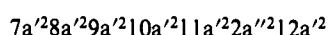
The DZ+P CISD wave functions for this electronic state include a total of 34 056 configurations, keeping seven core MOs doubly occupied and their counterpart virtual orbitals deleted. The TZ+P CISD wave functions include 65 695, in which only three virtual orbitals (1s core counterpart) are deleted. The TZ+2P basis set was not used for CISD investigations of this isomer. This compound may be regarded as the conjunction of the σ-bonded :Al—CH=ĊH[12] with a third H atom. The geometrical parameters and total energy of vinylaline are shown in Table V. The geometry is also described in Figure 3. The corresponding structural features for trans σ-bonded :Al—CH=ĊH, which is a minimum on the Al–C₂H₂ radical potential energy hypersurface, are also listed in Table V for the comparison. The dissociation energy of vinylaline (3) is 48.4 kcal/mol at the DZ+P SCF level. Like structures 1 and 2, the augmention of basis set makes the dissociation energy slightly smaller (43.9 kcal/mol for TZ+P SCF, and 44.2 kcal/mol for TZ+2P SCF), and the effects of electron correlation makes it larger (52.6 kcal/mol for DZ+P CISD, and 52.7 for CISD plus Davidson's correction; 47.5 kcal/mol for TZ+P CISD, and 47.7 for Davidson's correction). It is slightly surprising that the energy of vinylaline is even lower than that of the above-discussed two isomers, aluminirene (1) and ethynylalane (2), since the corresponding radical :Al—CH=ĊH is of higher energy than the three-membered-ring and HAl—C≡C—H radicals. This might be explained in light of the fact that C–H

Table VI. Theoretical Harmonic Vibrational Frequencies (cm⁻¹) for Vinylaline (Structure 3, Figure 3) at the SCF Level of Theory and Comparison with the Trans σ-Bonded Al–C₂H₂ Radical Complex with Infrared Intensities (km/mol) Given in Parentheses

sym	description	TZ+2P SCF	TZ+P SCF	DZ+P SCF	σ-bonded radical DZ+P SCFᵃ
a'	C–H stretch	3303 (22)	3299 (24)	3335 (32)	3335 (8)
a'	C–H stretch	3239 (14)	3227 (14)	3256 (16)	3253 (16)
a'	C–H stretch	3225 (30)	3216 (39)	3244 (48)	
a'	C–C stretch	1740 (12)	1738 (14)	1741 (15)	1681 (53)
a'	C–H bend	1537 (28)	1536 (27)	1535 (28)	
a'	C–H bend	1391 (1)	1390 (1)	1386 (1)	1249 (9)
a''	CH₂ twist	1157 (14)	1150 (16)	1144 (18)	
a''	CH₂ wag	1113 (38)	1113 (37)	1103 (41)	1001 (71)
a'	C–H bend	1053 (0.1)	1054 (0.4)	1052 (0.4)	969 (37)
a'	Al–C stretch	604 (119)	600 (121)	606 (122)	604 (140)
a''	Al–C wag	391 (4)	398 (4)	396 (5)	498 (0.6)
a'	Al–C bend	169 (3)	178 (3)	174 (3)	169 (6)

ᵃEarlier theoretical predictions.[12]

bonding energies are usually larger than Al–H bond energies.[23,24]

The predicted geometries for vinylaline at different levels of theory are in good agreement with each other. The deviations of most bond lengths are within the range of about 0.01 Å. Similar to the predictions for isomers 1 and 2, correlation effects shorten the Al–C bond length by 0.005 Å, and the extension of basis set lengthens it by 0.005 Å from DZ+P to TZ+P. The Al–C bond length in the structure :Al–R is 1.984–1.994 Å, which is much longer than predicted for 1 and 2. It is even longer than the experimentally characterized Al–C bond length in trimethylaluminum (1.957 Å) by 0.029–0.039 Å.

Harmonic vibrational frequencies for vinylaline at the SCF level of theory are shown in Table VI. The results are essentially in agreement among DZ+P, TZ+P, and TZ+2P basis sets. The strongest band is located at 604 cm⁻¹ with intensity 119 km/mol at the TZ+2P level (600 cm⁻¹, 121 km/mol at TZ+P, and 606 cm⁻¹, 122 km/mol with DZ+P), corresponding to the a' Al–C stretch mode. It is very close to the strongest band (also a' Al–C stretch mode) in trans σ-bonded Al–C₂H₂ complex. There are a couple of other strong fundamentals (with intensities more than 30 km/mole), such as the a'' CH₂ wag mode at 1113 cm⁻¹ at the TZ+2P level (1113 cm⁻¹ at TZ+P and 1103 cm⁻¹ at DZ+P) and the a' C–H stretch mode at 3225 cm⁻¹ at the TZ+2P level (3216 cm⁻¹ at TZ+P and 3244 cm⁻¹ at DZ+P). The C=C stretch for vinylaline is no longer a strong absorption band, the IR intensity

(23) Streitwieser, A.; Heathcock, C. A. *Introduction to Organic Chemistry*, 3rd ed.; Macmillan: New York, 1985; p 288.

(24) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

Table VII. Geometries and Energies of Aluminirane (Structure 4, Figure 4) and Comparison with the Three-Membered-Ring Al–C₂H₄ Radical (Results in Parentheses Are at the SCF Level, and Those Appearing First Are at the CISD Level of Theory)

	H–Al–C₂H₄ aluminirane (C_{2v})			Al–C₂H₄ $(^2A_1)$ 3-membered ring
	TZ+2P	TZ+P	DZ+P	DZ+Pᵃ
Al–H, Å	(1.564)	1.555 (1.561)	1.556 (1.561)	
Al–C, Å	(1.901)	1.907 (1.905)	1.906 (1.904)	1.925 (1.919)
C–C, Å	(1.603)	1.596 (1.600)	1.600 (1.600)	1.600 (1.595)
C–H, Å	(1.079)	1.086 (1.083)	1.090 (1.084)	1.090 (1.084)
C–C–H, deg	(114.0)	114.2 (114.1)	114.2 (114.1)	114.3 (114.3)
H–C–H, deg	(110.1)	109.8 (109.7)	109.7 (109.7)	110.0 (110.0)
E, hartree	(−320.49763)	−320.84667 (−320.49128)	−320.83064 (−320.48919)	−320.20853 (−319.88555)
E(Davidson), hartree		−320.88809	−320.87031	−320.24525
ΔE,ᵇ kcal·mol⁻¹	(−2.3)	6.9 (−2.4)	8.5 (−0.5)	
ΔE(Davidson),ᵇ kcal·mol⁻¹		7.0	8.4	

ᵃ Earlier theoretical predictions.[11]   ᵇ $\Delta E = E(\text{AlH} + \text{C}_2\text{H}_4) - E(\text{aluminirane})$.

Table VIII. Theoretical Harmonic Vibrational Frequencies (cm⁻¹) for Aluminirane (Structure 4, Figure 4) at the SCF Level and Comparison with the Three-Membered-Ring Al–C₂H₄ Radical with Infrared Intensities (km/mol) Given in Parentheses

sym	description	TZ+2P SCF	TZ+P SCF	DZ+P SCF	$^2A_1$ AlC₂H₄ DZ+P SCFᵃ
b₂	C–H stretch	3287 (21)	3276 (21)	3301 (32)	3306 (35)
a₂	C–H stretch	3266 (0)	3256 (0)	3281 (0)	3285 (0)
a₁	C–H stretch	3224 (19)	3210 (20)	3231 (29)	3233 (36)
b₁	C–H stretch	3214 (19)	3200 (20)	3220 (27)	3221 (31)
a₁	Al–H stretch	2061 (154)	2072 (180)	2072 (186)	
a₁	CH₂ scissors	1554 (1)	1548 (1)	1549 (1)	1549 (0.2)
b₁	CH₂ scissors	1536 (<0.1)	1528 (<0.1)	1528 (<0.1)	1529 (0.2)
a₂	CH₂ twist	1285 (0)	1280 (0)	1279 (0)	1271 (0)
b₁	CH₂ wag	1120 (0.3)	1126 (0.2)	1125 (0.1)	1064 (4)
a₁	CH₂ wag	1048 (8)	1057 (8)	1056 (8)	1044 (12)
a₁	C–C stretch	939 (8)	950 (11)	961 (11)	951 (4)
b₂	CH₂ twist	897 (74)	903 (78)	903 (75)	861 (2)
b₁	Al–C stretch	696 (130)	699 (66)	706 (141)	677 (92)
b₂	CH₂ rock	694 (65)	697 (139)	700 (71)	662 (11)
a₁	Al–C stretch	649 (8)	653 (7)	661 (8)	649 (12)
b₁	Al–H bend	544 (67)	542 (89)	543 (89)	
b₂	Al–H wag	422 (69)	431 (81)	430 (80)	
a₂	CH₂ rock	348 (0)	370 (0)	366 (0)	339 (0)

ᵃ Earlier theoretical predictions.[11]

being 12, 14, or 15 km/mol, while that predicted for the trans σ-bonded radical is 53 km/mol.

AlC₂H₅ Systems

Let us now turn to the hydrogenated aluminum–ethylene molecular systems, i.e. AlC₂H₅. The species that is analogous to structure **1** is aluminirane
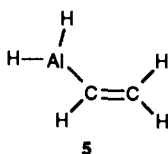
H
|
Al
/ \
H"··C——C··''H
/   \
H   H

4
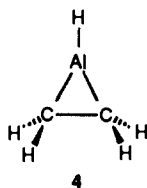
Its electron configuration with core molecular orbitals included implicitly) is

$5a_1^2 3b_2^2 2b_1^2 6a_1^2 7a_1^2 1a_2^2 8a_1^2 4b_2^2$
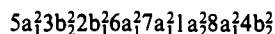
The present theoretical results are summarized in Tables VII and VIII and Figure 4.

A second low-lying isomer of AlC₂H₅ is vinylalane (C_s)

H
/
H—Al   H
\   /
C══C
/   \
H   H

5

The predicted geometrical parameters, energies, and vibrational frequencies of **5** are shown in Tables IX and X and Figure 5. In order to compare vinylalane with a corresponding open-shell
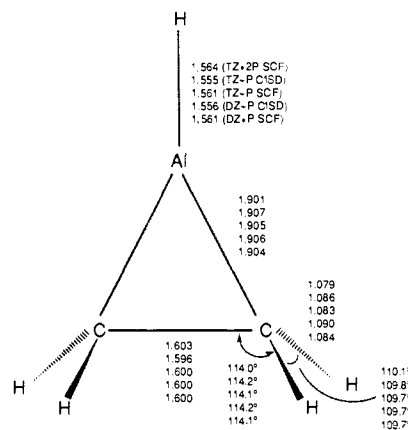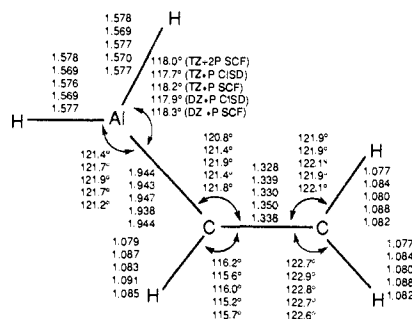
Figure 4. Ab initio equilibrium geometries for the aluminirane (structure **4**) molecule. All bond distances are in angstroms.

Figure 5. Ab initio equilibrium geometries for the vinylalane (structure **5**) molecule. All bond distances are in angstroms.

Table IX. Geometries and Energies of Vinylalane (Structure 5, Figure 5, Which Gives the Connectivity of the Distinct C and H Atoms) and Comparison with Vinylalene Radical (Results in Parentheses Are at the SCF Level, and Those Appearing First Are at the CISD Level of Theory)

|	vinylalane			vinylalene radical
	TZ+2P	TZ+P	DZ+P	DZ+P
Al–H, Å	(1.578)	1.569 (1.576)	1.569 (1.577)	1.581 (1.587)
Al–H, Å	(1.578)	1.569 (1.577)	1.570 (1.577)	
Al–C, Å	(1.944)	1.943 (1.947)	1.938 (1.944)	1.950 (1.954)
C–C, Å	(1.328)	1.339 (1.330)	1.350 (1.338)	1.350 (1.337)
C–H, Å	(1.079)	1.087 (1.083)	1.091 (1.085)	1.093 (1.085)
C–H, Å	(1.077)	1.084 (1.080)	1.088 (1.082)	1.088 (1.082)
C–H, Å	(1.077)	1.084 (1.080)	1.088 (1.082)	1.089 (1.082)
C–Al–H, deg	(121.4)	121.7 (121.9)	121.7 (121.2)	118.9 (118.7)
C–Al–H, deg	(118.0)	117.7 (118.2)	117.9 (118.3)	
C–C–Al, deg	(120.8)	121.4 (121.9)	121.4 (121.8)	123.0 (123.1)
C–C–H, deg	(116.2)	115.6 (116.0)	115.2 (115.7)	115.1 (115.6)
C–C–H, deg	(121.9)	121.9 (122.1)	121.9 (122.1)	121.9 (122.2)
C–C–H, deg	(122.7)	122.9 (122.8)	122.7 (122.6)	122.6 (122.5)
E, hartree	(−320.54145)	−320.88077 (320.53541)	−320.86335 (−320.53127)	−320.23186 (−319.92002)
E(Davidson), hartree		−320.92101	−320.90198	−320.26682
ΔE,ᵃ kcal·mol,ᵃ	(25.1)	28.3 (25.3)	29.0 (25.9)	
ΔE(Davidson),ᵃ kcal·mol⁻¹		27.7	28.3	

ᵃ $\Delta E = E(\text{AlH} + C_2H_4) - E(\text{vinylalane})$.

Table X. Theoretical Harmonic Vibrational Frequencies (cm⁻¹) for Vinylalane (Structure 5, Figure 5) at the SCF Level of Theory and Comparison with the Vinylalene Complex with Infrared Intensities (km/mol) Given in Parentheses

sym	description	TZ+2P SCF	TZ+P SCF	DZ+P SCF	vinylalene radical DZ+P SCF
a′	C–H stretch	3329 (15)	3322 (18)	3358 (25)	3357 (24)
a′	C–H stretch	3262 (14)	3253 (16)	3282 (20)	3280 (27)
a′	C–H stretch	3248 (17)	3240 (18)	3268 (25)	3260 (22)
a′	Al–H stretch	2012 (141)	2020 (153)	2020 (154)	1963 (254)
a′	Al–H stretch	2007 (225)	2015 (239)	2015 (252)	
a′	C–C stretch	1754 (18)	1752 (21)	1756 (23)	1755 (10)
a′	CH₂ bend	1546 (41)	1543 (40)	1541 (40)	1539 (28)
a′	C–H bend	1404 (1)	1400 (1)	1396 (1)	1392 (1)
a″	CH₂ twist	1158 (10)	1150 (16)	1144 (20)	1141 (21)
a″	CH₂ wag	1135 (46)	1134 (41)	1125 (44)	1121 (41)
a′	CH₂ bend	1094 (14)	1092 (14)	1089 (13)	1084 (16)
a′	Al–H bend	850 (350)	852 (391)	860 (392)	
a′	Al–C stretch	681 (33)	681 (35)	686 (34)	703 (180)
a″	Al–H wag	674 (326)	683 (373)	683 (375)	
a′	Al–H bend	557 (84)	561 (83)	563 (85)	590 (39)
a″	C–H wag	447 (0.2)	448 (0.3)	447 (0.2)	480 (29)
a′	AlCC bend	233 (1)	235 (1)	233 (1)	258 (3)
a″	Al–H wag	173 (<0.1)	179 (<0.1)	181 (<0.1)	186 (6)

Al–C₂H₄ radical, we also considered the ²A′ C–H insertion product radical
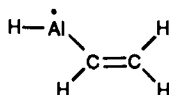
at the DZ+P SCF and CISD levels and report its energy and geometry in Table IX too. Perhaps surprisingly this C–H insertion product radical has never been considered in previous theoretical studies.[11] The electronic ground state for this radical corresponds to configuration

$$7a'^2 8a'^2 9a'^2 10a'^2 11a'^2 12a'^2 2a''^2 13a'$$
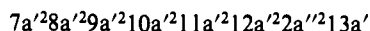
There are 53 323 configurations in the DZ+P CISD wave functions for this electronic state, when freezing seven core MOs and the seven highest virtual MOs. This AlC₂H₄ radical lies 12.4 kcal/mol (DZ+P CISD) or 9.7 kcal/mol (DZ+P SCF) lower in energy than the supermolecule Al + C₂H₄. Thus the ethylene insertion product lies energetically lower than any of the AlC₂H₄ isomers studied previously.[11]

Since structure 3 is the global minimum of AlC₂H₃, it is anticipated that the analogous structure of AlC₂H₅, namely ethylaline
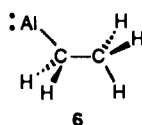
6
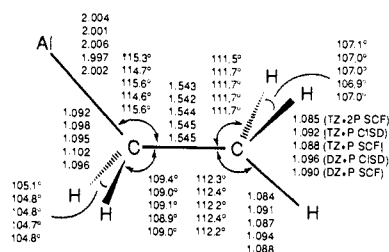
Figure 6. Ab initio equilibrium geometries for the ethylaline (structure 6) molecule. All bond distances are in angstroms.

might be the global minimum among AlC₂H₅ systems. The ethylaline ground-state electronic configuration (with core included implicitly) is

$$7a'^2 8a'^2 2a''^2 9a'^2 10a'^2 3a''^2 11a'^2 12a'^2$$
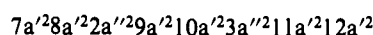
The theoretical predictions for ethylaline are summarized in Tables XI and XII and Figure 6.

Concluding Remarks

We have theoretically investigated three hydrogenated aluminum-acetylene isomers AlC₂H₃ and three hydrogenated aluminum-ethylene isomers AlC₂H₅. The geometries were fully optimized at the DZ+P (SCF and CISD), TZ+P (SCF and CISD), and TZ+2P SCF levels of theory. Some structures were

Table XI. Geometries and Energies of Ethylaline (Structure 6, Figure 6, Which Gives the Connectivity of the Distinct C and H Atoms) (Results in Parentheses Are at the SCF Level, and Those Appearing First Are at the CISD Level of Theory)

	TZ+2P	TZ+P	DZ+P
C-Al, Å	(2.004)	2.001 (2.006)	1.997 (2.002)
C-C, Å	(1.543)	1.542 (1.544)	1.545 (1.545)
C-H, Å	(1.092)	1.098 (1.095)	1.102 (1.096)
C-H, Å	(1.084)	1.091 (1.087)	1.094 (1.088)
C-H, Å	(1.085)	1.092 (1.088)	1.096 (1.090)
C-C-Al, deg	(115.3)	114.7 (115.6)	114.6 (115.6)
C-C-H, deg	(109.4)	109.0 (109.1)	108.9 (109.0)
H-C-H, deg	(105.1)	104.8 (104.8)	104.7 (104.8)
C-C-H, deg	(112.3)	112.4 (112.2)	112.4 (112.2)
C-C-H, deg	(111.5)	111.7 (111.7)	111.7 (111.7)
H-C-H, deg	(107.1)	106.9 (107.0)	106.9 (107.0)
E, hartree	(-320.54161)	-320.88826 (-320.53695)	-320.87213 (-320.53505)
E(Davidson), hartree		-320.93001	-320.91212
ΔE,[a] kcal·mol^{-1}	(25.3)	33.0 (26.2)	34.6 (28.3)
ΔE(Davidson),[a] kcal·mol^{-1}		33.3	34.7

[a] $\Delta E = E(\text{AlH} + C_2H_4) - E(\text{ethylaline})$

Table XII. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) for the Ethylaline (Structure 6, Figure 6) at the SCF Level of Theory with Infrared Intensities (km/mol) Given in Parentheses

sym	description	TZ+2P SCF	TZ+P SCF	DZ+P SCF
a′	C-H stretch (-CH$_3$)	3201 (37)	3200 (40)	3230 (53)
a″	C-H stretch (-CH$_3$)	3193 (50)	3191 (54)	3220 (69)
a′	C-H stretch (-CH$_3$)	3147 (40)	3140 (45)	3162 (55)
a″	C-H stretch (-CH$_2$-)	3117 (24)	3117 (24)	3138 (31)
a′	C-H stretch (-CH$_2$-)	3090 (36)	3087 (40)	3104 (50)
a″	C-H bend (-CH$_3$)	1635 (7)	1627 (8)	1627 (8)
a′	C-H bend (-CH$_3$)	1617 (2)	1610 (2)	1611 (2)
a′	C-H bend (-CH$_2$-)	1553 (4)	1549 (4)	1548 (4)
a′	C-H bend (-CH$_3$)	1531 (6)	1527 (7)	1527 (8)
a″	C-H bend (-CH$_2$-)	1351 (1)	1348 (2)	1346 (2)
a′	C-H bend (-CH$_2$-)	1323 (8)	1324 (11)	1324 (12)
a′	C-C stretch	1019 (21)	1029 (18)	1045 (15)
a′	C-H bend (-CH$_3$)	998 (13)	1002 (16)	1002 (20)
a″	C-H bend (-CH$_3$)	953 (9)	952 (10)	951 (11)
a′	C-Al stretch	557 (60)	562 (59)	566 (59)
a″	H$_2$AlC-CH$_3$ torsion	519 (6)	528 (7)	524 (7)
a″	C-Al bend (out-of-plane)	178 (2)	183 (2)	182 (2)
a′	C-Al bend (in-plane)	168 (3)	172 (3)	170 (3)

also characterized at the TZ+2P CISD level. All six isomers are predicted to be minima, lying below their respectively AlH + C$_2$H$_2$ and AlH + C$_2$H$_4$ dissociation limits.

For hydrogenated aluminum–acetylene, the dissociation energies of isomers 1, 2, and 3 are 26.6, 41.9, and 48.4 kcal/mol, respectively, relative to separated AlH and C$_2$H$_2$ at the DZ+P SCF level. The dissociation energies are decreased when the basis set augmented to the TZ+P level (22.0, 40.0, and 43.9 kcal/mole respectively), but they are somewhat increased when the basis set is further augmented to the TZ+2P level (i.e. 24.1, 40.3, and 44.2 kcal/mol, respectively). When the correlation energy is taken into account (CISD in this paper), the dissociation energies are increased to 32.8, 44.4, and 52.6 kcal/mol for the DZ+P basis set and to 27.7, 42.1, and 47.5 kcal/mol for the TZ+P basis set.

The global minimum of AlC$_2$H$_3$, at all levels of theory, is vinylaline (structure 3), which does not incorporate a Al-H bond but has three C-H bonds.

For AlC$_2$H$_5$, there are three analogous isomers; again all three are minima. The dissociation energies are −0.5, 25.9, and 28.3 kcal/mol respectively for isomers 4, 5, and 6 relative to AlH and C$_2$H$_4$ at the DZ+P SCF level. When the basis set is augmented, the dissociation energies are decreased to −2.4, 25.3, and 26.2 kcal/mol for the TZ+P basis set and −2.3, 25.1, and 25.3 kcal/mol for the TZ+P basis set. When correlation energy is taken into account (CISD in this paper), the D_e values are increased to 8.5, 29.0, and 34.6 kcal/mol for the DZ+P basis set and 6.9, and 28.3, and 33.0 kcal/mol for the TZ+P basis set. The global minimum is ethylaline (structure 6), the energy of which is 26.1 kcal/mol below the cyclopropane structure 4, and 4.7 kcal/mol below structure 5 at the TZ+P CISD level.

Generally speaking, the dissociation energies increase when correlation effects are considered and decrease when the basis set is augmented. The geometrical parameters of all the closed-shell compounds are reasonably close to standard values, except for several bond lengths within the three-membered-ring structures, which make the Al–C bonds shorter and the C—C or C=C bonds longer.

The theoretical harmonic vibrational frequencies of all six isomers are real, confirming that each is a genuine minimum on its potential energy hypersurface. It is anticipated it should be possible to prepare one or more of these closed-shell compounds in the laboratory. The predicted harmonic vibrational frequencies and their infrared intensities should be helpful in their identification, although theoretical harmonic frequencies at the DZ+P, TZ+P, or TZ+2P SCF levels of theory are expected to be 8–12% higher than the observed fundamentals.