The Wealth of Energetically Low-Lying Isomers for Very Simple Organometallic Systems. The Aluminum–Acetylene (AlC_2H_2) System

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Abstract: Ab initio molecular quantum mechanics has been used to predict the molecular structures, energetics, and vibrational frequencies of the plausible isomers of AlC_2H_2. Standard double-ζ plus polarization (DZ+P) basis sets have been used in conjunction with self-consistent field (SCF) and single- and double-excitation configuration interaction (CISD) methods. Of the eight different isomeric electronic states considered, the two lowest lying energetically are predicted to be nearly degenerate. The aluminum–vinylidene structure $AlCCH_2$ is predicted to be bound by D_e = 28 kcal/mol relative to infinitely separated aluminum atom plus acetylene. The second isomer results from insertion of the aluminum atom into one of the two C–H bonds of acetylene, i.e., HAlCCH, and lies 27 kcal (DZ+P Davidson unlinked cluster corrected CISD) below Al + C_2H_2. The third isomer of AlC_2H_2 is a three-membered ring structure (two distinct Al–C single bonds) of $^2A_1$ symmetry, lying 21 kcal below the asymptotic limit. The Dewar–Chatt–Duncanson π-complex follows energetically and is predicted to lie 19 kcal below Al + C_2H_2. The σ-bonded isomers (cis and trans) AlHCCH correspond to regions of the potential energy hypersurface energetically close to the π-bonded complex. However, only the trans structure remains a minimum at the DZ+P CISD level of theory. This trans $^2A'$ electronic state has a dissociation energy of 17 kcal/mol. The cis σ-bonded structure collapses to the π-bonded structure. A final isomer H_2AlCC is predicted to lie 16 kcal/mol above the dissociation limit Al + C_2H_2. These ab initio energetic predictions are compared to a simple empirical bond energy–bond order model. Vibrational frequencies and dipole moments are predicted for all minima with both DZ+P SCF and CISD methods.

In 1977 Kasai, McLeod, and Watanabe[1] reported the detection of the aluminum atom–acetylene adduct in neon matrices at 4 K via electron spin resonance (ESR) techniques. Although led by intuition to expect the π-bonded complex

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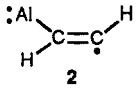
their experiments appeared to indicate otherwise. Specifically, the ^{27}Al hyperfine structure strongly suggested the presence of two nonequivalent protons. Accordingly, Kasai, McLeod, and Watanabe[1] proposed the σ-bonded molecular structure



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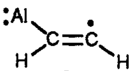
with the two hydrogen atoms lying trans with respect to each other.

The first theoretical study of the AlC_2H_2 system was reported in the 1979 paper by Trenary, Casida, Brooks, and Schaefer.[2] These authors not only considered structures **1** and **2** but also the cis σ-bonded structure



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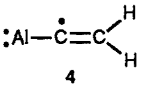
and the vinylidene structure



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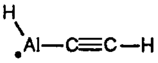
Although metal–vinylidene structures were scarcely known at the time,[3] the 1979 theoretical study showed clearly that **4** lies energetically below **1**–**3**.

Kasai reported a second experimental study[4] of the AlC_2H_2 system in 1982. Kasai suggested that the σ-bonded structure with hydrogens cis to each other is formed initially but that the lower trans structure can be produced by photoirradiation. Kasai did not comment on why the vinylidene structure predicted by ab initio theory[2] to lie lower is apparently not observed at all.

The latter point was addressed in the 1985 theoretical study by Scheiner and Schaefer.[5] These authors explicitly examined the barrier height for the unimolecular rearrangement of the σ-bonded **2** to the lower energy vinylidene structure **4**. This barrier is at least 30 kcal/mol, clearly prohibitive to isomerization under Kasai's experimental conditions, namely 4 K. This large activation energy would appear to explain why the global minimum vinylidene structure **4** is not observed in the ESR experiments.

A number of important unresolved questions remain for the AlC_2H_2 system. Perhaps first is why the π-bonded structure is not observed in the experiments of Kasai, McLeod, and Watanabe.[1,4] The π-bonded structure is observed for the related AlC_2H_4 system[4,6-9] and is bound by a least 16 kcal/mol.[9] Moreover, for the AlC_2H_4 system, theory has recently shown[10] that the σ-bonded structures collapse to the lower energy π-bonded minimum. Why does this happen for AlC_2H_4 but apparently not for AlC_2H_2? Moreover, it became clear during the course of our recent study[10] of the AlC_2H_4 system that there are a number of other isomers of AlC_2H_2 that have never been considered previously. One of these, the product of aluminum insertion into one of the C–H bonds, is a strong candidate for the AlC_2H_2 *global minimum*.



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Theoretical Approach

The standard basis set used in this research was of double-ζ plus polarization (DZ+P) quality. Specifically the atomic contracted Gaussian basis sets may be designated Al(11s7p1d/6s4p1d),[11,12] C(9s5p1d/

[†] Contribution CCQC No. 52.

(1) Kasai, P. H.; McLeod, D.; Watanabe, T. *J. Am. Chem. Soc.* **1977**, *99*, 3522.

(2) Trenary, M.; Casida, M. E.; Brooks, B. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1979**, *101*, 1638.

(3) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7764.

(4) Kasai, P. H. *J. Am. Chem. Soc.* **1982**, *104*, 1165.

(5) Scheiner, A. C.; Schaefer, H. F. *J. Am. Chem. Soc.* **1985**, *107*, 4451.

(6) Kasai, P. H.; McLeod, D. *J. Am. Chem. Soc.* **1975**, *97*, 5609.

(7) Howard, J. A.; Mile, B.; Tse, J. S.; Morris, H. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3701.

(8) Chenier, J. H. B.; Howard, J. A.; Mile, B. *J. Am. Chem. Soc.* **1987**, *109*, 4109.

(9) Mitchell, S. A.; Simard, B.; Rayner, D. M.; Hackett, P. A. *J. Phys. Chem.* **1988**, *92*, 1655.

(10) Xie, Y.; Yates, B. F.; Yamaguchi, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1989**, *111*, 7239.

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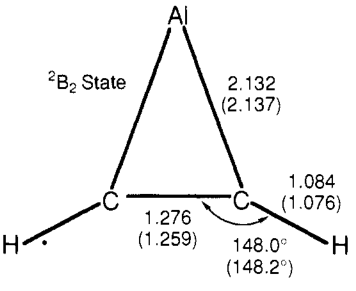

Figure 1. Ab initio equilibrium geometries for the $^2B_2$ electronic ground state of π-bonded AlC_2H_2 (**1**). The DZ+P CISD geometrical parameters are given first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.

4s2p1d),[13,14] and H(4s1p/2s1p).[13,14] Chosen polarization function orbital exponents were $\alpha_d(Al) = 0.4$, $\alpha_d(C) = 0.75$, and $\alpha_p(H) = 0.75$. 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[15,16] for open-shell systems. The CI wave functions included all Hartree–Fock interacting[17,18] single and double excitations (CISD) with respect to the single-configuration SCF wave function.

The ^2P_u electronic ground state of the aluminum atom is spatially 3-fold degenerate. For perpendicular approaches of Al to C_2H_2 the ^2P_u atomic state resolves into C_{2v} states of $^2A_1$, $^2B_1$, and $^2B_2$ symmetry. The Hartree–Fock wave functions for these three states have the qualitative form (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):

$$5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 8a_1^2 9a_1 \qquad {}^2A_1 \tag{1}$$

$$5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 8a_1^2 3b_1 \qquad {}^2B_1 \tag{2}$$

$$5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 8a_1^2 4b_2 \qquad {}^2B_2 \tag{3}$$

In the CISD wave functions, the seven corelike SCF MO's (1s2s2p Al and 1s C) are constrained to be double-occupied in all configurations. Similarly the seven highest virtual orbitals (core counterparts for a DZ quality basis set) are deleted from the CI procedure. In this way, with the DZ+P basis set, there are 13 241 configurations for the $^2B_1$ state and 14 042 configurations for the $^2B_2$ state.

For the σ-bonded *trans*-**2** and *cis*-**3** structures, of $^2A'$ symmetry, the self-consistent field electron configurations are the same, namely

$$7a'^2 8a'^2 9a'^2 10a'^2 2a''^2 11a'^2 12a' \tag{4}$$

In a manner analogous to that described above, the DZ+P CISD wave functions include a total of 27 947 configurations in C_s symmetry. Structure **5**, the result of Al atom insertion into one of the acetylene C–H bonds, also is described by (4) within the Hartree–Fock approximation.

Among the isomers mentioned in the introduction, the vinylidene structure **4** corresponds to electron configuration

$$6a_1^2 7a_1^2 2b_2^2 8a_1^2 2b_1^2 9a_1^2 3b_2 \tag{5}$$

The DZ+P CISD wave functions for the $^2B_2$ ground state of the vinylidene isomer include a total of 14 230 configurations in C_{2v} symmetry.

Conventional Perpendicular Approach of ^2P_u Al to Acetylene

The qualitative considerations discussed in Swope's 1976 paper[19] suggest (see Swope's Figure 3) that the $^2B_2$ potential energy curve should be most attractive as Al approaches C_2H_2 in a perpendicular manner. The $^2B_1$ curve should be less attractive and the $^2A_1$ curve repulsive.

The above qualitative predictions were borne out by our ab initio results for AlC_2H_2. The DZ+P SCF and CISD equilibrium geometries for the $^2B_2$ state (structure **1**) are displayed in Figure 1. As expected, the $^2B_2$ electronic state is tightly bound compared to the $^2B_1$ state, with predicted Al–C distance 2.132 Å (DZ+P CISD). This distance represents a bond somewhat weaker than a conventional aluminum–carbon single bond. For example the Al–C distance (2.132 Å) in the present π-bonded complex is 0.175 Å longer than that determined experimentally[20] (1.957 Å) for monomeric trimethylaluminum in the gas phase.

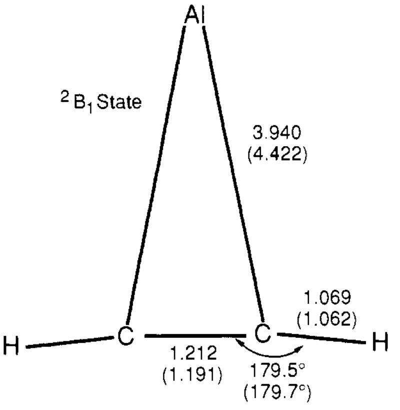

Figure 2. Weakly bound $^2B_1$ electronic state of π-bonded AlC_2H_2 (**6**). The DZ+P CISD structural parameters are given first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.

Also of interest is the distortion of the acetylene molecule within the AlC_2H_2 complex. For comparison, we have carried out a CISD geometry optimization for the supermolecule in which acetylene is separated by 100 bohrs from the aluminum atom. The C_2H_2 structure thus obtained (DZ+P CISD) is

$$r_e(C{\equiv}C) = 1.212\ \text{Å} \qquad r_e(C{-}H) = 1.069\ \text{Å}$$

Parenthetically, we note that the above theoretical structure agrees reasonably well with the experimental[21] equilibrium structure of acetylene: $r_e(C{\equiv}C) = 1.203$ Å, $r_e(C{-}H) = 1.062$ Å.

In light of the above, there is significant lengthening of the C≡C triple bond in acetylene upon π-complexation with the Al atom. Specifically, the C≡C distance increases by 0.064 Å from the free acetylene (1.212 Å) to AlC_2H_2 (1.276 Å). The best qualitative description of the carbon–carbon bond in the $^2B_2$ ground state of π-bonded AlC_2H_4 is as a weak (or long) C≡C bond.

Another geometrical parameter of interest is the bending-back angle of the CH groups with respect to the collinear free acetylene molecule. For the $^2B_2$ ground state of π-bonded AlC_2H_2 this bending-back angle is 31.8° at the DZ+P SCF and 32.0° at the DZ+P CISD level of theory. It is seen that the attachment of the Al atom causes a significant nonlinearity in the acetylene molecule.

Since recent experiments[9] suggest a dissociation energy $D_0(AlC_2H_4) \geq 16$ kcal/mol, the analogous quantity for AlC_2H_2 is of special interest. DZ+P SCF theory predicts a smaller dissociation energy, namely 8.3 kcal/mol. However, DZ+P CISD increases the value, yielding a dissociation energy of 17.0 kcal/mol. When the Davidson correction[22] for the effects of certain (i.e., unlinked clusters) quadruple excitations is appended, the predicted dissociation energy is 18.5 kcal/mol. At each level of theory the AlC_2H_2 dissociation energies are larger than those predicted[10] by the same method for AlC_2H_4. The Davidson-corrected DZ+P CISD prediction for the latter is 11.6 kcal/mol, or 6.9 kcal less than predicted here for AlC_2H_2. We conclude that acetylenes form a significantly stronger π-complex with aluminum than does ethylene. It seems reasonable that the main difference between the AlC_2H_2 and AlC_2H_4 ring structures is that the acetylene

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(11) Huzinaga, S. Approximate Atomic Wavefunctions. II. Department of Chemistry Report; University of Alberta: Edmonton, AB, 1971.

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

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

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

(15) Goddard, J. D.; Handy, N. C.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *71*, 1525.

(16) Osamura, Y.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1981**, *75*, 2919.

(17) Bunge, A. *J. Chem. Phys.* **1970**, *53*, 20.

(18) Bender, C. F.; Schaefer, H. F. *J. Chem. Phys.* **1971**, *55*, 4798.

(19) Swope, W. C.; Schaefer, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 7962.

(20) Almenningen, A.; Halvorsen, S.; Haaland, A. *Acta Chem. Scand.* **1971**, *25*, 1937.

(21) Baldacci, A.; Ghersetti, S.; Hurlock, S. C.; Rao, K. N. *J. Mol. Spectrosc.* **1976**, *59*, 116.

(22) Davidson, E. R. *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; D. Reidel: Dordrecht, Holland, 1974; pp 17–30.

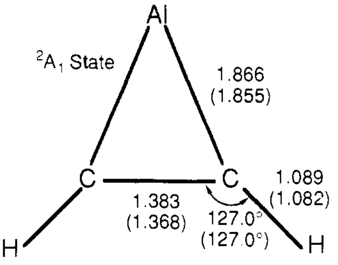
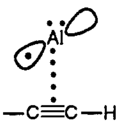


Figure 3. Conventional three-membered-ring structure ($^2A_1$ symmetry, **7**) for AlC_2H_2. Note that this structure incorporates two Al–C single bonds. The DZ+P CISD geometrical parameters are given first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.

species can donate π-electrons into the formally empty p π AO of aluminum. Incidentally, this makes **7** formally a 2π-aromate.

The DZ+P SCF and CISD equilibrium geometries for the $^2B_1$ π-bonded electronic state



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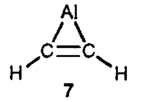
are displayed in Figure 2. As expected from the qualitative ideas of Swope,[19] the $^2B_1$ AlC_2H_2 complex is very weakly bound. The SCF, CISD, and Davidson-corrected CISD dissociation energies D_e are 0.2, 0.7, and 0.8 kcal/mol, respectively. This very weak binding is reflected in Figure 2 by an acetylene geometry that is very little changed from C_2H_2 in vacuo. Specifically, the C=C distance is 1.212 Å (less than 0.001 Å longer than for free C_2H_2) and the C–H bending-back angle is only 0.5°. Accordingly, the Al–C distance is very long, 3.940 Å with DZ+P CISD.

As expected,[19] the $^2A_1$ potential energy surface is repulsive as ^2P_u Al approaches acetylene. Nevertheless, after pushing over a barrier, one finds a minimum (structure **3**) in this potential curve corresponding to a different electron configuration from (2). This new $^2A_1$ electron configuration is

$$5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 4b_2^2 8a_1 \qquad (6)$$

Further, it must be emphasized that **3** is low-lying energetically, unlike the analogous electronic state[10] of AlC_2H_4. With the DZ+P basis set, the latter structure lies 11.9 (SCF), 2.3 (CISD), and 1.7 kcal (Davidson-corrected CISD) *above* separated Al + C_2H_4. In striking contrast, the analogous $^2A_1$ state of AlC_2H_2 is predicted to be significantly bound, by 14.3 (DZ+P SCF), 20.9 (DZ+P CISD), and 20.9 kcal (Davidson-corrected DZ+P CISD). This antithesis between the AlC_2H_2 and AlC_2H_4 binding energies for the three-membered ring structures is the greatest single difference found here between the acetylene and olefin systems.

The $^2A_1$ structure



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is also of particular interest because it incorporates two conventional aluminum–carbon single bonds. As seen in Figure 3 the DZ+P CISD Al–C bond distances are 1.866 Å, notably shorter than for the experimentally characterized[20] trimethylaluminum, for which r(Al–C) = 1.957 Å. In fact, these Al–C bond distances are 0.05 Å shorter than found for any of the eight structures examined here. Furthermore, the predicted C—C distance (1.383 Å) is significantly longer than the standard C=C double-bond value[10] of 1.34 Å. This $^2A_1$ structure is probably most representative of the closed-shell three-membered ring system. The latter system, for which no experimental data yet exist, should have two fairly normal Al–C single bonds. Presumably, the ground-state electron configuration for closed-shell $HAlC_2H_2$ will simply add one electron to the $8a_1$ orbital of electron configuration (6).

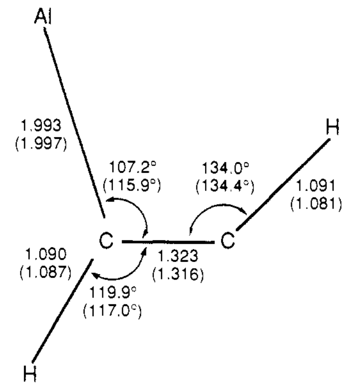


Figure 4. Trans vinyl radical-like (σ-bonded) state of AlC_2H_2 (**2**). This is the equilibrium geometry stated to be observed in the ESR experiments of Kasai, McLeod, and Watanabe.[1,4] The DZ+P CISD geometrical parameters are given first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.

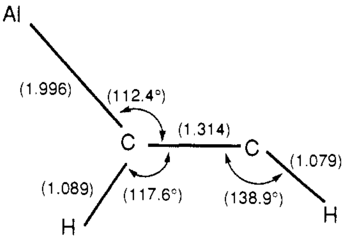


Figure 5. σ-Bonded state of AlC_2H_2 having the two hydrogen atoms cis to each other (**3**). The DZ+P SCF geometrical parameters are given in parentheses. There is no DZ+P CISD structure. At this higher level of theory the cis structure collapses to π-bonded $^2B_2$ state **1**.

An alternative to our view of structure **7** as a three-membered ring compound is suggested by the 1986 paper of Koch, Frenking, Gauss, Cremer, Sawaryn, and Schleyer.[31] Their global minimum for the C_2Be molecule is also an apparent three-membered ring with a C–Be distance that is also smaller than the standard value r(C–Be). However, Koch's analysis of the electron density distribution shows that there is little electron density between the C and Be atoms. Rather, the structure is characterized by a T-shaped electron density distribution. The same analysis might also be applicable to **7**. Thus, it is conceivable that interatomic distance is not a sufficient criterion for labeling **7** as a cyclic structure.

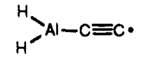
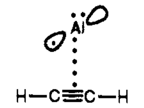
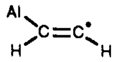
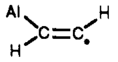
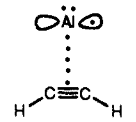
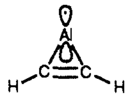
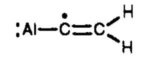
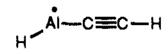
σ-Bonded Vinyl Radical-like Structures

As suggested elsewhere,[1,2,5] the present theoretical study predicts conformation **2** with the hydrogen atoms trans to each other to lie lower. Figure 4 shows the DZ+P SCF and CISD equilibrium molecular structures for the trans-σ-bonded conformation. The predicted equilibrium geometry is qualitatively similar to that reported earlier in lower level theoretical studies.[2,5] The theoretical dissociation energies for the trans-σ-bonded structure are 11.9 kcal (SCF), 15.1 kcal (CISD), and 16.5 kcal (Davidson).

The cis-σ-bonded structure **3** is depicted in Figure 5. The DZ+P SCF equilibrium geometry is qualitatively similar to the earlier reported DZ SCF structure.[2,5] However, when one attempts to optimize the cis structure at the DZ+P CISD level of theory, the structure collapses to π-bonded $^2B_2$ electronic state **1**. This result is contrary to the interpretation that Kasai, McLeod, and Watanabe gave to their ESR experiments and requires a careful analysis.

The theoretical predictions concerning the interplay between π-bonded ($^2B_2$), trans-σ-bonded, and cis-σ-bonded structures vary dramatically on going from DZ+P SCF to DZ+P CISD. At the SCF level of theory, the ab initio results are completely consistent with the experimental interpretation of Kasai, McLeod, and Watanabe.[1,4] That is, both cis- and trans-σ-bonded vinyl radi-

Table I. Summary of Relative Energies (kcal/mol) for the AlC_2H_2 System[a]

			relative energy		
no.	structure		SCF	CISD	Davidson-corrected CISD
8		$^2A_1$ RC_2 radical	+19.0	+17.5	+16.6
6		$^2B_1$ perpendicular	-0.2	-0.7	-0.8
3		$^2A'$ cis-σ-bonded	-11.6	collapses[b]	
2		$^2A'$ trans-σ-bonded	-11.9	-15.1	-16.5
1		$^2B_2$ π-bonded	-8.3[c]	-17.0	-18.5
7		$^2A_1$ three-membered ring	-14.3	-20.9	-20.9
4		$^2B_2$ vinylidene	-25.3	-27.3	-27.9
5		$^2A'$ C-H insertion product	-25.8	-27.8	-27.1
	$Al + C_2H_2$	dissociation limit $Al + C_2H_2$	0.0	0.0	0.0

[a] All theoretical predictions were made with a double-ζ plus polarization (DZ+P) basis set. Unless indicated, all structures are minima on their respective potential energy surfaces [b] Collapses to the lower energy $^2B_2$ π-bonded state at this level of theory. [c] This structure is a transition state at this level of theory.

cal-like structures are minima, with the trans structure lying lower. With the DZ+P SCF method, the π-bonded $^2B_2$ structure is not a minimum, but rather a transition state connecting two equivalent cis-σ-bonded structures. The SCF binding energies relative to separated $Al + C_2H_2$ are 8.3 kcal (π-bonded), 11.6 kcal (cis-σ-bonded), and 11.9 kcal (trans-σ-bonded).

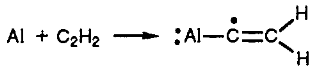
The above harmony between theory and experiment vanishes when the effects of electron correlation are included in the different wave functions. As seen in Table I, the π-bonded structure becomes a minimum at the DZ+P CISD level of theory and lies *lower in energy* than either the cis or trans structures. Furthermore, as noted above, the cis structure is not a stationary point at all with the DZ+P CISD method. The trans-σ-bonded structure (D_e = 15.1 kcal) lies 1.9 kcal above the π-bonded $^2B_2$ state (D_e = 17.0 kcal) at this level of theory. When the Davidson correction[22] is appended, both D_e values increase, to 16.5 kcal (trans) and 18.5 kcal ($^2B_2$).

The following picture emerges at the DZ+P CISD level of theory. The lowest energy structure observed in collisions between Al and acetylene at 4 K should be π-bonded $^2B_2$ electronic state **1**. The fact that this state is apparently not observed in the Kasai experiments[1,4] is puzzling. The σ-bonded trans structure **2** should also be observed, as reported by Kasai, McLeod, and Watanabe.[1,4] However, this structure is predicted to lie 2 kcal/mol above the Dewar–Chatt–Duncanson complex. Higher levels of theory will be necessary to precisely establish the energetic relationship between the π-bonded $^2B_2$ and σ-bonded trans structures.

Aluminum–Vinylidene Structures

The DZ+P SCF and CISD equilibrium structures for structure **4** are shown in Figure 6. The aluminum–carbon bond distance from DZ+P CISD is 1.953 Å, actually a bit shorter than the earlier reported[5] DZ SCF prediction, 1.971 Å. This Al–C single-bond distance is virtually indistinguishable from the experimental value for trimethylaluminum.

The predicted dissociation energies (in order of increasing reliability) for the aluminum–vinylidene structure are seen in Table I to be 25.3 kcal (SCF), 27.3 kcal (CISD), and 27.7 kcal (Davidson corrected). This is the first significantly bound AlC_2H_2 structure for which correlation effects do not significantly increase the predicted dissociation energy. As shown earlier[2,5] the vinylidene isomer lies energetically below the σ-bonded cis and trans isomers and the π-bonded $^2B_2$ structure. The reason the vinylidene isomer is not observed in the ESR experiments is the barrier (~20 kcal[5]) for the reaction



(7)

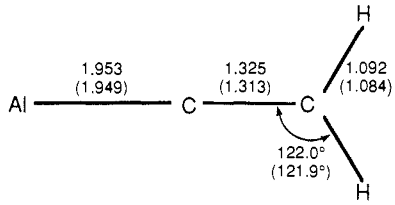


Figure 6. Aluminum-vinylidene isomer (**4**) of the AlC_2H_2 system. The DZ+P CISD geometrical parameters are given first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.

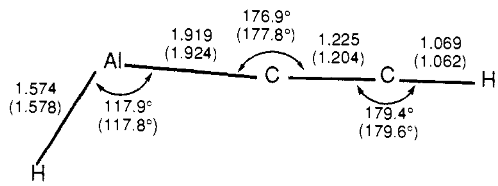


Figure 7. C–H insertion product of the reaction of atomic aluminum with acetylene (**5**). The DZ+P CISD geometrical parameters are given first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.

The C–H Insertion Product

A very low-lying AlC_2H_2 structure never previously considered is **5**, which results from the insertion of the aluminum atom into

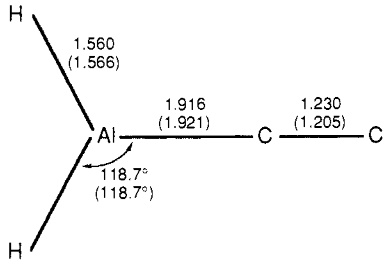


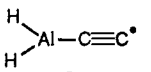
Figure 8. AlC_2H_2 isomer of the form of the class of radicals $RC_2^{\bullet}$. This predicted equilibrium geometry is structure **8** in the text and is high-lying energetically. The DZ+P CISD geometrical parameters are given first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.

one of the two C–H bonds of acetylene. Figure 7 gives the DZ+P SCF and CISD structures for this C–H insertion product. The Al–C distance in **5** is 1.919 Å, or 0.038 Å shorter than observed[20] for the prototype Al–C single bond in trimethylaluminum. The carbon–carbon bond distance is predicted to be 1.225 Å (DZ+P CISD), only 0.013 Å longer than for isolated acetylene at the same level of theory. It is apparent that the C≡C triple bond is preserved in insertion product **5**.

Table I shows that the predicted dissociation energies D_e for the C–H insertion product are 25.8 kcal (DZ+P SCF), 27.8 kcal (DZ+P CISD), and 27.1 kcal (Davidson-corrected CISD). Clearly this isomer of AlC_2H_2 is potentially observable. At the most reliable level of theory for relative energies (Davidson-corrected DZ+P CISD), C–H insertion product **5** lies only 0.8 kcal above vinylidene structure **4**. The theoretical method used is not sufficiently reliable to guarantee that this energetic ordering might not reverse itself with a larger basis set or more complete treatment of electron correlation. Nevertheless, it is manifest that **4** and **5** are nearly degenerate and that both are rather strongly bound.

$RC_2^{\bullet}$ Radical Structure

Structure **5**, which incorporates a reasonable unadulterated C≡C triple bond, is very low-lying energetically. This observation leads one to attempt to visualize other structures retaining the C≡C moiety. The only remaining such candidate is



8

which is related to the C_2H radical. Replacing the H atom in C_2H by the AlH_2 radical yields structure **8**.

The predicted equilibrium geometry **8** is shown in Figure 8. The C≡C triple bond remains largely intact, albeit 0.018 Å longer than for isolated acetylene. The Al–C bond is a somewhat short single bond (1.916 Å) by comparison with the standard trimethylaluminum (1.957 Å). Thus, the theoretical molecular structure is consistent with classification as an $RC_2^{\bullet}$ radical.

Table I shows that structure **8** is not a contender for the AlC_2H_2 global minimum. In fact, it is evident that **8** lies energetically above separated Al + C_2H_2. Nevertheless, our vibrational analysis will show that the $H_2AlC_2^{\bullet}$ isomer is a true minimum on both the DZ+P SCF and CISD potential energy hypersurfaces. This is not surprising since one cannot readily imagine a simple pathway for dissociation to Al + C_2H_2.

Attempted Rationalization of Isomeric Energetics

Given the mass of energetic data in Table I, it is reasonable to ask whether a simple model might provide a framework of explanation for these theoretical predictions. The obvious course of action is to see to what degree these detailed ab initio predictions may be justified in terms of a simple bond energy–bond order picture.

For this purpose, we assume the following average bond energies: C—H, 99 kcal; C═C, 146 kcal; C≡C, 200 kcal; Al—H, 70 kcal; Al—C, 75 kcal. The first three values may be obtained from current organic chemistry texts.[23] The Al–H bond energy is from the diatomic molecule,[24] and the Al–C bond energy is a theoretical prediction.[25]

In such a simple picture the energy content of separated Al + C_2H_2 is 398 kcal/mol. The vinylidene structure $AlCCH_2$ is empirically estimated to lie 21 kcal lower. The Davidson-corrected DZ+P CISD dissociation energy for vinylidene structure **4** is actually 27.9 kcal, and we would increase this by 5–10 kcal is asked for our best guess. Thus, either the Al—C single bond or the C═C double bond is somewhat stronger than suggested by simple bond energy arguments.

The same empirical bond energy strategy suggests that C–H insertion product **5** $HAlC_2H$ should lie 46 kcal below Al + C_2H_2. Our highest level ab initio prediction for this dissociation energy is 27.1 kcal, but a value as large as 46 kcal is conceivable. Otherwise the strengths of the Al–H or Al–C bonds may be overestimated a bit by the simple model.

Both σ-bonded structures, *trans*-**2** and *cis*-**3**, are predicted by the empirical model to be degenerate with vinylidene structure **4**. This is because all three isomers have one Al—C, one C═C, and two C—H bonds. In fact, the ab initio methods predict the cis structure not to be a minimum and the trans structure to lie 11.4 kcal above the vinylidene structure. The actual dissociation energy suggested for all three structures (21 kcal) by the empirical model is very close to a reasonable extrapolation from the Davidson-corrected DZ+P CISD value (16.5 kcal) for the trans structure.

At this point the empirical model begins to fail more seriously. This simple method has no way to estimate the energy of π-bonded $^2B_2$ state **1**, since there is no standard Al···C π-bonded energy. Three-membered ring structure **7** is predicted to be bound by 96 kcal/mol relative to Al + C_2H_2. The fact that ab initio theory gives 21 kcal may, however, be rationalized in terms of ring strain. Perhaps more puzzling is the $H_2AlC_2^{\bullet}$ structure, which is predicted by the model to lie 17 kcal below Al + C_2H_2. In fact this structure lies *higher* in energy than Al + C_2H_2. This bonding arrangement must weaken either the C≡C triple bond or the Al—C single bond or both.

Might on adjust the Al–C and/or Al–H bond energies, for which there are no "standard" values, to better accommodate the best ab initio predictions? A plausible suggestion might be to lower the Al–H value by 5 kcal, to 65 kcal. This would cause $RC_2^{\bullet}$ radical **8** to lie only 7 kcal below Al + C_2H_2, in much better agreement with the theoretical prediction that this species lies slightly above Al + C_2H_2. The same adjustment would bring the HAlCCH D_e estimate down to 41 kcal, also in better agreement with theory. This simple standard bond energy model is helpful in causing us to ponder the energetic relationships between the different isomers of AlC_2H_2. However, its inadequacies prove that such a model is no substitute for detailed theoretical or experimental studies.

Vibrational Frequencies

Although no experimental study of the infrared spectrum of the AlC_2H_2 system has yet appeared, there is an unpublished report of the IR spectrum of the related aluminum–ethylene system, by Manceron and Andrews.[26] Furthermore, Andrews[27] has already begun an analogous matrix isolation IR study of the AlC_2H_2 system. Thus, a principal goal of this study was to provide reliable theoretical predictions of the expected IR spectra of the AlC_2H_2 isomers. The only previous information of this sort are DZ SCF predictions for only the vinylidene and σ-bonded isomers. Also the earlier, lower level theoretical study[5] did not include infrared intensities.

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[23] Streitweiser, A.; Heathcock, C. A. *Introduction in 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.

[25] Fox, D. J.; Ray, D.; Rubesin, P. C.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *73*, 3246.

[26] Manceron, L.; Andrews, L. Infrared Spectrum and Structure of the AlC_2H_4 Molecule in Solid Argon, Symposium on Molecular Structure and Spectroscopy, Columbus, OH, June 1988; Abstract MH1.

[27] Andrews, L. Personal communication, March 27, 1989.

Table II. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) for the Aluminum–Vinylidene Isomer of AlC_2H_2 (Structure **4**), with Infrared Intensities (km/mol) Given in Parentheses

symmetry	description	DZ+P SCF	DZ+P CISD
b_1	C–H stretch	3329 (10)	3247 (8)
a_1	C–H stretch	3254 (18)	3172 (14)
a_1	C–C stretch	1810 (60)	1729 (37)
a_1	CH_2 scissors	1515 (31)	1450 (16)
b_2	CH_2 wag	1067 (39)	954 (37)
b_1	CH_2 rock	1018 (2)	950 (0.7)
a_1	Al–C stretch	544 (161)	535 (134)
b_2	AlCC bend (out-of-plane)	215 (4)	186 (3)
b_1	AlCC bend (in-plane)	180 (8)	176 (7)

Table III. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) for the C–H insertion Product of the Reaction of Atomic Aluminum with Acetylene (Structure **5**), with Infrared Intensities (km/mol) Given in Parentheses

symmetry	description	DZ+P SCF	DZ+P CISD
a'	C–H stretch	3617 (38)	3524 (32)
a'	C–C stretch	2248 (63)	2122 (51)
a'	Al–H stretch	1996 (210)	1987 (176)
a''	H–C–C–Al torsion	848 (44)	822 (40)
a'	CCH bend	798 (55)	690 (71)
a'	CAlH bend	665 (261)	645 (212)
a'	Al–C stretch	594 (61)	585 (46)
a'	AlCC bend	240 (11)	213 (9)
a''	C–C–Al–H torsion	230 (15)	203 (11)

Table IV. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) for Three-Membered Ring Structure **7** of AlC_2H_2, with Infrared Intensities (km/mol) Given in Parentheses

symmetry	description	DZ+P SCF	DZ+P CISD
a_1	C–H stretch	3326 (28)	3251 (30)
b_1	C–H stretch	3306 (18)	3230 (18)
a_1	C–C stretch	1496 (0.4)	1432 (0.6)
b_1	C–H bend	1258 (25)	1158 (13)
a_2	C–H wag	1097 (0)	1017 (0)
a_1	C–H bend	1016 (1)	963 (2)
a_1	Al–C stretch	809 (62)	780 (41)
b_1	Al–C stretch	713 (53)	685 (58)
b_2	C–H wag	706 (145)	634 (126)

Table V. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) for the $^2B_2$ Electronic Ground State of π-Bonded AlC_2H_2 (Structure **1**), with Infrared Intensities (km/mol) Given in Parentheses

symmetry	description	DZ+P SCF	DZ+P CISD
a_1	C–H stretch	3418 (3)	3331 (2)
b_1	C–H stretch	3360 (8)	3275 (4)
a_1	C–C stretch	1870 (7)	1789 (7)
a_1	C–H bend	863 (21)	828 (16)
b_1	C–H bend	606 (34)	752 (51)
a_2	C–H wag	779 (0)	711 (0)
b_2	C–H wag	643 (104)	589 (90)
a_1	Al–C stretch	479 (86)	480 (74)
b_1	Al–C stretch	$234i$	349 (3)

DZ+P SCF and DZ+P CISD harmonic vibrational frequencies and IR intensities are given in Tables II–IX. The CI results were obtained via finite differences of analytic CISD gradients. This necessitates going to lower symmetries than required for the geometry optimizations. Nevertheless, the sizes of the CISD expansions are modest; for the C–H insertion product HAlCCH in C_1 symmetry, for example, the number of configurations is 50 947.

Table VI. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) for the Trans Vinyl Radical-like (σ-Bonded) State of AlC_2H_2 (Structure **2**), with Infrared Intensities (km/mol) Given in Parentheses

symmetry	description	DZ+P SCF	DZ+P CISD
a'	C–H stretch	3335 (8)	3248 (2)
a'	C–H stretch	3253 (16)	3216 (8)
a'	C–C stretch	1681 (53)	1613 (33)
a'	C–H bend	1249 (9)	1146 (12)
a''	C–H wag	1001 (71)	929 (63)
a'	C–H bend	969 (37)	882 (71)
a'	Al–C stretch	604 (140)	605 (122)
a''	AlCH wag	498 (0.6)	426 (0.0004)
a'	Al–C bend	169 (6)	136 (4)

Table VII. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) for the Cis Vinyl Radical-like (σ-Bonded) State of $Al-C_2H_2$ (Structure **3**), with Infrared Intensities (km/mol) Given in Parentheses[a]

symmetry	description	DZ+P SCF
a'	C–H stretch	3359 (6)
a'	C–H stretch	3221 (15)
a'	C–C stretch	1670 (37)
a'	C–H bend	1234 (36)
a''	C–H wag	951 (4)
a'	C–H bend	907 (13)
a'	Al–C stretch	602 (122)
a''	AlCH wag	471 (51)
a'	Al–C bend	145 (2)

[a] This table does not include DZ+P CISD results because, as described in the text, the cis structure collapses to the π-bonded $^2B_2$ state **1** at this higher level of theory.

Table VIII. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) for the Weakly Bound $^2B_1$ State (Perpendicular Approach) of AlC_2H_2 (Structure **6**), with Infrared Intensities (km/mol) Given in Parentheses

symmetry	description	DZ+P SCF	DZ+P CISD
a_1	C–H stretch	3675 (0.1)	3577 (0.3)
b_1	C–H stretch	3569 (99)	3481 (86)
a_1	C–C stretch	2202 (0.7)	2079 (1)
a_1	C–H bend	861 (135)	773 (120)
b_2	C–H wag	855 (106)	762 (89)
b_1	C–H bend	770 (0.03)	627 (0.03)
a_2	C–H wag	766 (0)	(0)
b_1	Al–C stretch	45 (0.2)	49 (0.3)
a_1	Al–C stretch	24 (0.3)	44 (0.8)

Table IX. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) for the $H_2AlC_2^{\bullet}$ or $RC_2^{\bullet}$ Radical Structure **8** of AlC_2H_2,[a] with Infrared Intensities (km/mol) Given in Parentheses

symmetry	description	DZ+P SCF	DZ+P CISD
a_1	C–C stretch	2300 (28)	2138 (22)
a_1	Al–H stretch	2061 (108)	2069 (206)
b_1	Al–H stretch	2060 (238)	2061 (94)
a_1	AlH_2 scissors	854 (424)	838 (403)
b_2	AlH_2 wag	669 (365)	648 (314)
a_1	Al–C stretch	609 (73)	600 (66)
b_1	AlH_2 rock	592 (110)	558 (77)
b_2	AlCC bend (out-of-plane)	223 (1)	162 (0.5)
b_1	AlCC bend (in-plane)	219 (0.4)	142 (0.003)

[a] This structure is actually predicted to lie above separated Al + C_2H_2.

Among the significantly bound isomers, vinylidene **4** and C–H insertion product **5** lie lowest. The vinylidene IR predictions are seen in Table II. From DZ SCF[5] to DZ+P CISD (present work), the predicted C–H stretching frequencies decrease from 3360 to 3247 cm^{-1} (b_1) and 3272 to 3172 cm^{-1} (a_1). Typical errors in harmonic vibrational frequencies for stable closed-shell molecules are +3.7% at the DZ+P CISD level of theory.[28] Of course the observed fundamentals will also reflect the effects of anharmonicity, and this will probably reduce the harmonic frequencies by a further 2–5%.

For vinylidene structure **4**, the Al–C stretching frequency (535 cm^{-1}) is predicted to be quite intense (134 km/mol) in the infrared spectrum. The observation of such an Al–C stretch would be of considerable interest. Also significantly allowed are the C=C

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(28) Besler, B. H.; Scuseria, G. E.; Scheiner, A. C.; Schaefer, H. F. *J. Chem. Phys.* **1988**, *89*, 360.

stretch at 1729 cm^{-1} (37 km/mol) and the CH_2 wag at 954 cm^{-1} (37 km/mol). The DZ+P CISD C=C stretch (1729 cm^{-1}) occurs very close to that predicted for isolated ethylene at the same level of theory[29] (1737 cm^{-1}). Of course, the C=C stretch for ethylene is forbidden in the infrared.

Vibrational frequencies for C–H insertion product **5** are seen in Table III. The acetylene C–H harmonic stretch frequency is predicted at 3524 cm^{-1}, by far the highest of any of the significantly bound AlC_2H_2 isomers. For comparison, the extremely weakly bound $^2B_1$ state (Table VIII) displays a symmetric C–H stretch at 3577 cm^{-1} (DZ+P CISD). Thus, for HAlCCH, the C–H stretch is predicted to be downshifted by only 53 cm^{-1} compared to isolated acetylene. Since the observed[30] fundamental for HCCH is at 3372 cm^{-1}, we estimate that the true anharmonic C–H stretch for HAlCCH should lie at about 3372 - 53 = 3319 cm^{-1}. The observation of such a vibrational frequency (±30 cm^{-1}) for the AlC_2H_2 system would strongly point to the presence of the C–H insertion product HAlCCH, structure **5**.

The C≡C triple-bond stretch harmonic frequency (2122 cm^{-1}) for **5** actually lies 41 cm^{-1} *above* the analogous prediction for isolated acetylene. The IR intensity for this fundamental is 51 km/mol, while that for acetylene is, of course, identically zero. The Al–C stretching vibration is predicted to lie at 585 cm^{-1} (DZ+P CISD) in the harmonic approximation.

The Al–H stretch is predicted to be a very strong feature in the IR spectrum (176 km/mol). Structure **5** is the only low-lying isomer of AlC_2H_2 incorporating an Al–H bond. Moreover, the Al–H stretch at 1987 cm^{-1}, when empirically corrected[28] to ~1800 cm^{-1}, would be a signature for the HAlC≡CH isomer, since no other energetically low-lying AlC_2H_2 isomer is predicted to have a fundamental within 100 cm^{-1}.

Infrared parameters for three-membered ring structure **7** are given in Table IV. Except for the C—H wag at 634 cm^{-1}, with I = 126 km/mol, none of the fundamentals are predicted to be terribly intense. The C=C stretching frequency, perhaps of greatest interest, is predicted by both DZ+P SCF and CISD methods to be quite weak. It is, however, of interest that this nominal C=C double bond is predicted to have a stretching frequency 1737 - 1432 = 305 cm^{-1} below that of isolated ethylene at the same level of theory. This downshift in vibrational frequency may be correlated with a C=C bond distance (Figure 3) of 1.368 Å, about 0.03 Å longer than that predicted for isolated ethylene at the same level of theory.

Another unique feature of the three-membered ring IR spectra is the presence of the two Al–C motions at higher frequencies (780 and 685 cm^{-1}, DZ+P CISD, harmonic approximation) than for the other isomers. The higher frequencies are presumably due to the tightness of the three-membered ring environment. Both Al–C features have reasonable IR intensities (41 and 58 km/mol), and their relatively high Al–C vibrational frequencies might serve as signatures for the three-membered ring isomer.

Although the experimental studies of AlC_2H_2 are at a very preliminary stage, Andrews[27] has indicated that he may have observed the π-bonded structure **1**. This would of course be a surprise since it would be contrary to the conclusions of Kasai, McLeod, and Watanabe.[1,4] Our predictions for the $^2B_2$ IR spectrum are given in Table V. As expected for such a complex, the two frequencies associated with Al–C motion lie relatively low, at 480 and 349 cm^{-1}, respectively. The former is predicted to be strongly allowed in the IR, with DZ+P CISD intensity 74 km/mol. The same two vibrational frequencies for the aluminum–ethylene system lie even lower at 387 and 232 cm^{-1}. The downshifts from AlC_2H_2 to AlC_2H_4 are consistent with the ab initio dissociation energies, 18.5 kcal for AlC_2H_2 and 11.6 kcal for AlC_2H_4.

The trans-σ-bonded structure **2** is the highest in energy of the five plausible AlC_2H_2 ground-state contenders at the DZ+P CISD level of theory. The harmonic vibrational frequencies for structure **2** are given in Table VI. The largest predicted IR intensity (122 km/mol) is for the Al–C stretching frequency, which falls at 605 cm^{-1}. On the basis of the predicted C=C stretching frequency (1613 cm^{-1} for **2**, 1737 cm^{-1} for isolated C_2H_4 at the same level of theory[29]), there is no trace of the C≡C triple bond of the reactant acetylene molecule. Interestingly, the opposite picture emerges from the structural comparisons, which show that the C=C distance in the trans-σ-bonded complex is 1.323 Å, a bit less than the 1.339 Å predicted for isolated ethylene. Thus, the carbon–carbon bond order structure **2** is somewhat problematical, although in any case close to 2.0.

Concluding Remarks

The principal conclusion from this work is that there are at least five low-lying isomers of the AlC_2H_2 system. The three energetically lowest isomers, **4**, **5**, and **7**, have apparently never been observed in the laboratory. However, C–H insertion product **5** does possess two inequivalent hydrogen atoms, a key feature in the ESR spectrum of Kasai, McLeod, and Watanabe.[1,4]

The focus of past[1,4] and current experimental studies appears to be on structures **1** and **2**, which at the DZ+P CISD level of theory are predicted to be the fourth and fifth lowest lying isomers. However, **1** and **2** are readily accessible to low-energy collisions between atomic aluminum and acetylene, while structures **4**, **5**, and **7** may face significant activation energies from the Al + C_2H_2 side. A previous theoretical study[5] has shown that the barrier from Al + C_2H_2 to vinylidene structure **4** is substantial. As more experimental information concerning the AlC_2H_2 system becomes available, a careful examination of the barriers to **5** and **7** should be made.

A final point of interest concerns the polarities of the eight AlC_2H_2 structures. Vinylidene structure **4** has μ(DZ+P CISD) = 1.0 D, the C–H insertion product **5** has μ = 0.6 D, the three-membered ring **7** has μ = 1.3 D, π-complex **1** has μ = 1.5 D, trans-σ-bonded structure **2** has μ = 0.7 D, and $RC_2^\bullet$ radical **8** has μ = 0.7 D. Even the very weakly bound (less than 1 kcal with DZ+P CISD) $^2B_1$ state (perpendicular approach) develops a dipole moment of 0.4 D. For all structures except the very weakly bound state $^2B_1$ **6**, the aluminum atom may be thought of as carrying a positive charge in some simple picture of the electronic structure. Specifically the DZ+P SCF Mulliken atomic populations on aluminum range from +0.39 ($^2B_2$ π-bonded state **1**) to +0.70 (three-membered ring **7**). The $RC_2^\bullet$ structure **8**, predicted to lie above separated Al + C_2H_2, has an even larger Mulliken charge on Al, namely 0.98.

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(29) Lee, T. J.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 7062.

(30) Herzberg, G. *Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand: Princeton, 1967.

(31) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Sawaryn, A.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1986**, *108*, 5732–5737.