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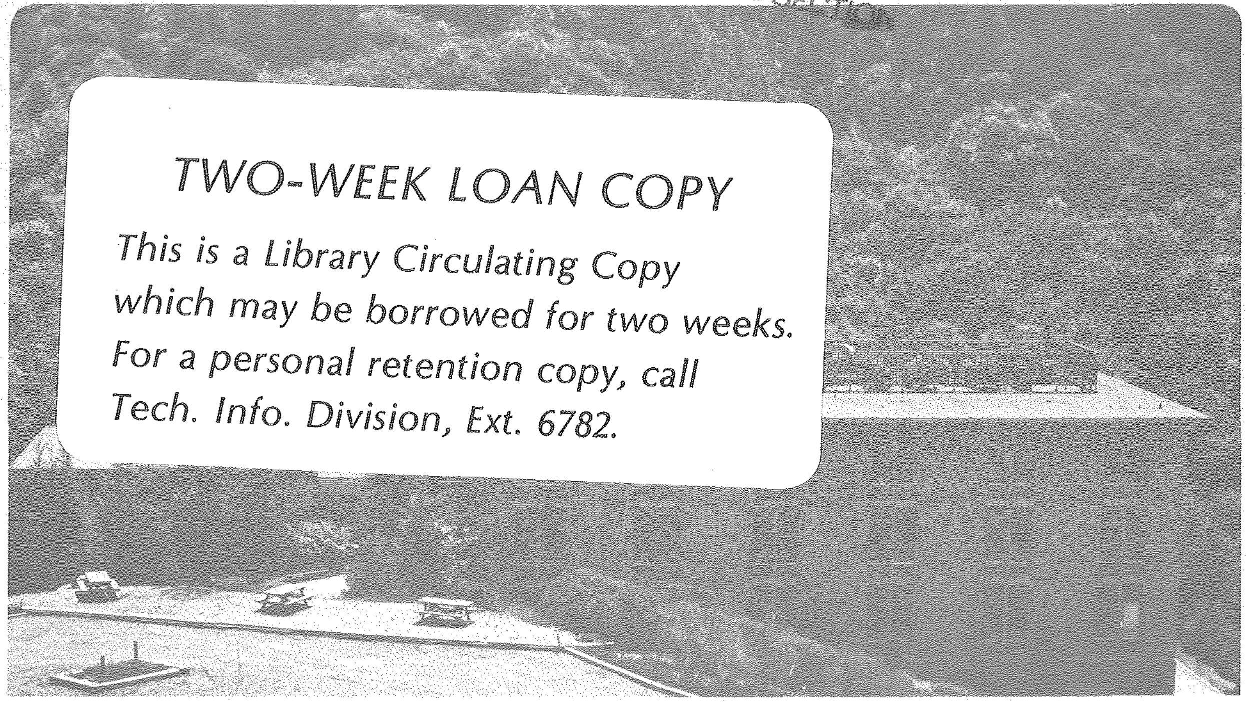

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The Prototype Aluminum - Carbon Single, Double, and Triple Bonds: $A\ell - CH_3$, $A\ell = CH_2$, and $A\ell \equiv CH$

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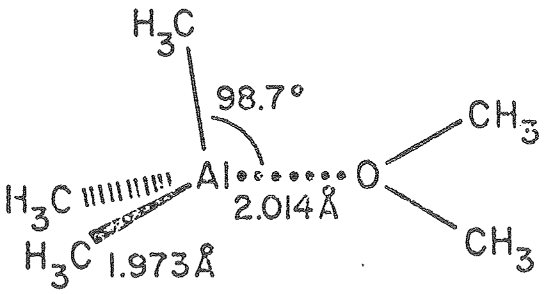
Abstract

Nonempirical quantum mechanical methods have been used to investigate the $A\ell CH_3$, $A\ell CH_2$, and $A\ell CH$ molecules, which may be considered to represent the simplest aluminum-carbon single, double, and triple bonds. Equilibrium geometries and vibrational frequencies were determined at the self-consistent-field level of theory using double zeta basis set: $A\ell$(11s7p/6s4p), C(9s5p/4s2p), H(4s/2s). The $^1A_1$ ground state of $A\ell CH_3$ has a reasonably conventional $A\ell$-C single bond of length 2.013 Å, compared to 1.96 Å in the known molecule $A\ell(CH_3)_3$. The CH equilibrium distance is 1.093 Å and the $A\ell$-C-H angle 111.9°. The structures of three electron states each of $A\ell CH_2$ and $A\ell CH$ were similarly predicted. The interesting result is that the ground state of $A\ell CH_2$ does not contain an $A\ell$-C double bond, and the ground state of $A\ell CH$ is not characterized by an $A\ell{\equiv}C$ bond. The multiply-bonded electronic states do exist but they lie 21 kcal ($A\ell CH_2$) and 86 kcal ($A\ell CH$) above the respective ground states. The dissociation energies of the three ground electronic states are predicted to be 68 kcal ($A\ell CH_3$), 77 kcal ($A\ell CH_2$), and 88 kcal ($A\ell CH$). Vibrational frequencies are also predicted for the three molecules, and their electronic structures are discussed with reference to Mulliken populations and dipole moments.

Introduction

After silicon, aluminum is the most abundant (8% by weight) metal in the earth's crust and is of considerable industrial importance owing to the fact that it is light, malleable, ductile, highly reflective, and resistant to oxidation.[1] Furthermore, organoaluminum compounds are used on an industrial scale as components of the Ziegler-Natta catalysts for olefin polymerization.[2] In the form of $LiA\ell H_4$, aluminum also plays a key role in synthetic organic and inorganic chemistry.[3] Although aluminum has a notable chemistry of its own,[4] this is primarily restricted to single bonded and/or electron-deficient species. A very useful example of the latter is the $A\ell_2(CH_3)_6$ molecule,[5] which has the diborane structure. However, a notable feature of aluminum is that to date the larger boron hydride analogues[6] such as $A\ell_5H_9(B_5H_9)$ have not been prepared.

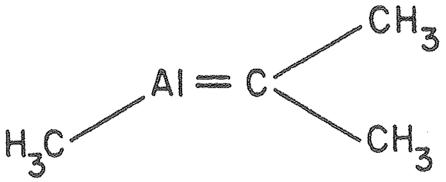
Perhaps the most common single-bonded organoaluminum species is the monomeric trimethyl aluminum, $A\ell(CH_3)_3$, the molecular structure of which has been determined by electron diffraction.[7] $A\ell(CH_3)_3$ has D_{3h} symmetry with freely rotating methyl groups and an Aℓ-C distance of 1.957 Å. The C-H distance is 1.113 Å and the Aℓ-C-H angle 111.7°. Since aluminum alkyls often appear in complexes with ethers, it is noteworthy that the structure of the dimethyl ether complex



has also been determined recently.[8]

Comparison with the above cited monomer structure demonstrates that complexation has only a mild effect (e.g. 0.016 Å in the Aℓ-C distance) on the free $A\ell(CH_3)_3$ geometry.

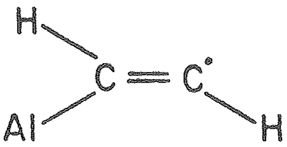
No aluminum-carbon multiple bond has yet been prepared in the laboratory. This is usually thought not to be due to the inability of molecules such as



(2)

to exist as isolated species. Rather, it seems likely that such molecules <u>do</u> represent relative minima on their respective potential energy surfaces, but are extremely reactive.[9] As such the structures and bond energies of these novel species are the proper domain of modern chemical theory. Such theoretical studies should in turn shed light on the possibility of observing such molecules in the laboratory.

The relevance of the aluminum-carbon double bond to experimental studies has already been demonstrated by the work of Trenary and coworkers.[10] They pursued the experimental conclusion of Kasai, McLeod, and Watanabe[11] (based on matrix isolation spectroscopy) that the σ-bonded



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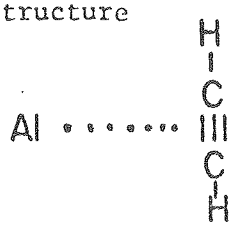
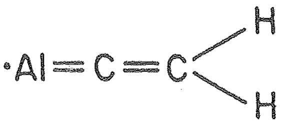
structure lies lower in energy than the more conventional[12] aluminum-acetylene π-bonded structure



(4)

Although the Kasai energetic ordering[11] was confirmed, the (nominally)

$A\ell{=}C$ double bonded structure



(5)

was predicted to lie $\sim$ 12 kcal lower than the σ-bonded radical (3). A plausible reconciliation between theory and experiment was based on the possible inability of (3) to rearrange to (5) under the 4° K conditions of the experiment.

In the present paper are reported theoretical studies of the prototype single, double, and triple bonds

$$:A\ell - CH_3 \tag{6}$$

$$\cdot A\ell = CH_2 \tag{7}$$

and

$$A\ell \equiv CH \tag{8}$$

$A\ell{-}CH_3$ is quite analogous to the spectroscopically characterized BH[13] and $A\ell H$[14] molecules and should be "makable." The prototype aluminum carbene (7) and aluminum carbyne (8) species bear less obvious resemblences to already known[15] molecules, but should be accessible in the near future via the rapidly expanding techniques of metal atom synthesis.[16] In addition to their obvious relation to fundamental organoaluminum chemistry, these three molecules may allow us to establish further the ill-defined relationship[17] between the former discipline and the world[18, 19] of heterogeneous catalysis and surface chemistry. The theoretical prediction of vibrational frequencies for the three prototype molecules may be particularly helpful[20] in that regard.

Theoretical Approach

The equilibrium geometrical structures of $A\ell CH_3$, $A\ell CH_2$, and $A\ell CH$ were initially determined at the self-consistent-field (SCF) level of theory. This was accomplished using a standard double zeta basis set for aluminum[21] $A\ell$(11s7p/6s4p), carbon[22] (9s5p/4s2p), and hydrogen[22] H(4s/2s). The energy minimization procedures were accelerated using closed and open shell gradient procedures described previously.[23,24] Also determined at the DZ SCF level were the quadratic force constants and subsequently the harmonic vibrational frequencies.

With the optimized geometries thus determined, several more complete levels of theory were explored. First, polarization functions were added to the basis set. These specifically included six primitive d-like $A\ell$ functions (d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{xz}, d_{yz}) with gaussian exponent $\alpha = 0.6$, an analogous set of carbon d functions with $\alpha = 0.75$, and a set of p functions ($\alpha = 1.0$) on each hydrogen atom. Such polarization functions are often critically important[25] in predictions of relative energies, e.g. dissociation energies and electronic excitation energies.

The effects of electron correlation were explicitly investigated using the loop-driven graphical unitary group approach.[26,27] The specific configuration interaction (CI) procedure used here included all singly- and doubly- excited configurations relative to the appropriate SCF reference configurations. For molecules of the size considered here, this type of CI will yield more than 90% of the valence shell correlation energy.[28] By constraining the six lowest ($A\ell$ 1s, 2s, 2p; C 1s) molecular SCF orbitals to be doubly occupied in all configurations, core and core-valence correlation effects were excluded. Furthermore, the six highest virtual orbitals, which are also localized in the core regions, were deleted from the CI. The largest CI reported here included 18, 491 configurations.

$A\ell$-CH_3 Results

Since the aluminum atom and the methyl radical each have a single unpaired electron, it is intuitively sensible to bring them together to form a conventional single bond. This is precisely the qualitative picture presented by Goddard and Harding[29] in their description of the closely related $A\ell H$ molecule.

As a preliminary step, the geometrical structure of the planar (D_{3h}) methyl radical in its $^2A_2''$ ground state was determined. At the DZ SCF level of theory the CH distance is 1.073 Å (in good agreement with Herzberg's experimental value [30] 1.079 Å) and the ground state electron configuration

$$1a_1'^2\ 2a_1'^2\ 1e'^4\ 1a_2'' \tag{9}$$

When resolved into the lower point group C_{3v} appropriate to the $A\ell$-CH_3 complex, (9) becomes

$$1a_1^2\ 2a_1^2\ 1e^4\ 3a_1 \tag{10}$$

The aluminum atom ground electron configuration

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p \tag{11}$$

becomes in C_{3v} symmetry either

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1e^4\ 4a_1^2\ 5a_1 \tag{12}$$

or

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1e^4\ 4a_1^2\ 2e \tag{13}$$

Of the two only (12) is suitable for engaging in a σ bond with the methyl radical, and the resulting $A\ell$-CH_3 electron configuration is

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 1e^4\ 5a_1^2\ 2e^4\ 6a_1^2\ 7a_1^2 \tag{14}$$

The predicted molecular structure of ground state $A\ell$-CH_3 is given in Figure 1. Of greatest interest is the aluminum-carbon distance, 2.0129 Å, which may be compared with the 1.957 Å determined experimentally for $A\ell(CH_3)_3$. The agreement is reasonable and it seems fair to conclude that the Aℓ-C bond in $A\ell$-CH_3 is a conventional single bond. The predicted equilibrium CH distance, 1.0925 Å, is 0.0196 Å longer than predicted for the isolated CH_3 radical. Furthermore, the Aℓ-C-H angle, which would be 90° if CH_3 retained its isolated planarity, is increased to 111.89° for the $A\ell$-CH_3 complex. Thus the structural evidence suggests that the CH_3 group in $A\ell$-CH_3 is much more similar to a methyl group in a saturated hydrocarbon than to the methyl free radical.

Given the $A\ell$-CH_3 equilibrium geometry, all quadratic force constants were predicted in terms of cartesian coordinates.[31] This 15 x 15 matrix was then diagonalized to yield the nine real, positive harmonic vibrational frequencies seen in Table I. The use of cartesian force constants for the $A\ell$-CH_3 molecule gives rise to an internal self-checking in that the three degenerate E vibrational modes should in fact be degenerate. In the present calculations this degeneracy was satisfied to within 1.2 cm^{-1} in every case. In addition, the six eigenvalues corresponding to translational and rotational degrees of freedom were satisfactorily small, namely 44, 23, 17, 1, -2, and -4 cm^{-1}. A further discussion of these vibrational frequencies will be postponed in order to examine all three molecules simultaneously.

Total energies for $A\ell CH_3$ are summarized in Table II. At the DZ SCF level of theory, the predicted Aℓ-C dissociation energy is 45.1 kcal/mole. This, of course, corresponds to independent geometrical optimations for $A\ell$-CH_3 and the separated asymptote Aℓ + CH_3. Using the larger DZ+P basis set, the SCF dissociation energy is 48.3 kcal/mole.

To predict the $A\ell$-CH_3 dissociation energy using configuration interaction (CI) methods is a bit more difficult.[32] This is because the SCF energy of (14) does not approach that of $A\ell + CH_3$ as the $A\ell$-C bond distance is lengthened. In this case configuration (14) dissociates to the closed-shell fragments $A\ell^+ + CH_3^-$. To obtain proper dissociation, of course, a two configuration SCF wave function of the form

$$\begin{aligned} &C_1 \ldots\ldots 5a_1^{\,2}\ 2e^4\ 6a_1^{\,2}\ 7a_1^{\,2} \\ +\ &C_2 \ldots\ldots 5a_1^{\,2}\ 2e^4\ 6a_1^{\,2}\ 8a_1^{\,2} \end{aligned} \qquad (15)$$

may be used. This two configuration SCF wave function yields $A\ell$-C dissociation energies of 52.6 (DZ basis set) and 56.9 (DZ+P) kcal/mole.

The straightforward way to predict the CI dissociation energy of $A\ell$-CH_3 is by including all single and double excitations with respect to both of the configurations in (15). This two reference configuration interaction (TRCI) description yields a double zeta dissociation energy of 60.2 kcal. With the larger DZ+P basis set, there are no fewer than 18,491 configurations, in C_s symmetry, making these among the largest CI calculations performed to date on our minicomputer. In this way the DZ+P TRCI dissociation energy was predicted to be 67.8 kcal, somewhat greater than the results obtained from the less complete levels of theory. Experience suggests[25] that this dissociation energy is probably still less than the (unknown) experimental D_e, which might be as much as 10 kcal greater. In this respect, it is noteworthy that the $A\ell$-CH_3 dissociation energy is quite comparable to the analogous binding energy[13], 70 kcal, of the $A\ell$-H molecule. This comparison may be placed in context by the observation that the C-C and C-H average single bond energies are 99 and 83 kcal. Thus, while C-H bonds are generally stronger than C-C single bonds, the diatomic $A\ell$-H bond is quite similar in this regard to the $A\ell$-C bond investigated here.

The $A\ell\text{-}CH_3$ molecule has a small but notable dipole moment, 0.56 debye at the DZ SCF level and 0.53 debye using the larger DZ+P basis set. Intuition suggests an $A\ell^{+\delta}CH_3^{-\delta}$ polarity and this is born out. The small magnitude of the $A\ell\text{-}CH_3$ dipole moment supports the contention (suggested above on the basis of structural data) that the $A\ell\text{-}C$ bond is a reasonably normal covalent single bond. Further data in this regard is given by the Mulliken population analysis seen in Table III. There it is seen that in the Mulliken picture[33] (using the DZ+P basis set) the charge distribution is $A\ell^{+0.55}CH_3^{-0.55}$, implying a considerable measure of ionicity. However, we view the dipole moment, which is a nonarbitrary physical observable, as more meaningful in this regard, and conclude that the bond in $A\ell\text{-}CH_3$ is best regarded as covalent. The $A\ell$ atom hydridization is $s^{1.9}p^{0.6}$ in this picture and polarization functions are seen to be of quantitative rather than qualitative importance.

$A\ell = CH_2$ Results

In analogy with formaldehyde ($O = CH_2$) or thioformaldehyde ($S = CH_2$), the doubly bonded $A\ell = CH_2$ species should have a planar C_{2v} structure. To construct the prerequisite σ and π bonds, it is perhaps easiest to begin with triplet methylene

$$1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\ 1b_1 \tag{16}$$

The $3a_1$ orbital is the σ orbital and the $1b_1$ orbital is generally called a π orbital. The DZ SCF structure of ${}^3B_1$ CH_2 was found to be $r_e(CH) = 1.074$ Å, $\theta_e(HCH) = 130.3°$, in reasonable agreement with more complete theoretical treatments.[34]

When the $A\ell$ atom ground state electron configuration (11) is resolved into C_{2v} symmetry, the threefold degeneracy of the singly occupied 3p orbital yields three distinct orbital occupancies:

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_1^2\ 1b_2^2\ 4a_1^2\ 5a_1 \tag{17}$$

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_1^2\ 1b_2^2\ 4a_1^2\ 2b_1 \tag{18}$$

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_1^2\ 1b_2^2\ 4a_1^2\ 2b_2 \tag{19}$$

To bring Aℓ up to CH_2 and form a double bond, it is clear that, in a simple picture, the Aℓ atom must have at least two unpaired electrons. The obvious choice is to use the Aℓ configuration

$$1s^2\ 2s^2\ 2p^6\ 3s\ 3p^2 \tag{20}$$

which is resolved in C_{2v} symmetry (maintaining three singly-occupied orbitals, as required to construct the Aℓ = C double bond) into three new configurations

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_1^2\ 1b_2^2\ 4a_1\ 5a_1\ 2b_1 \tag{21}$$

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_1^2\ 1b_2^2\ 4a_1\ 5a_1\ 2b_2 \tag{22}$$

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_1^2\ 1b_2^2\ 4a_1\ 2b_1\ 2b_2 \tag{23}$$

Given the singly-occupied $3a_1$ (σ) and $1b_1$ (π) orbitals of methylene, it is seen that either (21) or (23) may be used to create the desired Aℓ = CH_2 moiety. These two choices yield the electron configurations

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 1b_1^2\ 1b_2^2\ 5a_1^2\ 2b_2^2\ 6a_1^2\ 2b_1^2\ 7a_1 \tag{24}$$

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 1b_1^2\ 1b_2^2\ 5a_1^2\ 2b_2^2\ 6a_1^2\ 2b_1^2\ 3b_2 \tag{25}$$

In either case, the $6a_1$ orbital nominally contains the σ bond, and the $2b_1$ orbital the π bond.

Preliminary investigations were designed to determine whether the $^2A_1$ state (24) or $^2B_2$ state (25) is the lower lying of the two "double-bonded" electronic states. The structures of these two states are seen in Fig. 1, which demonstrates that both Aℓ-C bond distances are indeed less than the 1.95 Å normally associated with an Aℓ-C single bond. Of the two doubly-bonded states, the $^2A_1$ state (24) lies lower, with DZ SCF energy of -280.80072 hartrees. The Aℓ=C bond distance of 1.802 Å is seen to be 0.211 Å less than reported above for the single bond $A\ell\text{-}CH_3$ structure. Later comparison with the triply-bonded Aℓ≡CH confirms that this $^2A_1$ $A\ell CH_2$ structure is indeed characteristic of an Aℓ=C double bond. However, the higher-lying of the two states expected to manifest Aℓ=C bonds has at best a 3/2 bond, with AℓC distance 1.925 Å. The DZ SCF energy of the $^2B_2$ state is -280.6602 hartrees, or 84.5 kcal above the $^2A_1$ state, and thus rules out the $^2B_2$ state as a chemically significant species.

The actual ground electronic state of $A\ell CH_2$ does not contain an Aℓ=C double bond. Rather it arises from the electron configuration

$$1a_1^{\,2}\ 2a_1^{\,2}\ 3a_1^{\,2}\ 4a_1^{\,2}\ 1b_1^{\,2}\ 1b_2^{\,2}\ 5a_1^{\,2}\ 2b_2^{\,2}\ 6a_1^{\,2}\ 7a_1^{\,2}\ 2b_1 \qquad (26)$$

and is of $^2B_1$ symmetry. At the DZ SCF level of theory, the $^2B_1$ state is found to lie 32.9 kcal below the $^2A_1$ state. At the most reliable level of variational theory (DZ+P CI), this separation is reduced to 22.9 kcal. The structure of $^2B_1$ state is shown in Fig. 1 and the total energies at various levels of theory given in Table II. Figure 1 shows clearly that the AℓC bond in the ground $^2B_1$ state of $A\ell CH_2$ is a simple single bond. The Aℓ-C distance, 1.989 Å, is in fact only 0.024 Å shorter than that for the "standard" single bond in $A\ell CH_3$. This structural similarity is nicely complemented by the fact that the Mulliken populations (Table III) show essentially identical Aℓ atom hybridization and charge (+0.54) for the ground states of $A\ell CH_3$ and $A\ell CH_2$.

The methylene HCH bond angles for the three electronic states of $A\ell CH_2$ are of particular interest. In previous studies[17] of the related $MnCH_2$ system, a simple qualitative molecular orbital argument was found to explain several such methylene angles. Examination of the Walsh diagram for AH_2 molecules suggests that the $3a_1$ orbital plays the critical role. This orbital much prefers bent geometries, and comparison with experiment suggests the following:

$$3a_1^0\ \theta = 180°;\ 3a_1^1\ \theta \sim 133°;\ 3a_1^2\ \theta \sim 102°$$

By projecting out carbon and hydrogen atom a_1 populations from the $MnCH_2$ Mulliken analysis, this same simple picture qualitatively explained the $MnCH_2$ bond angles.

For the three $A\ell CH_2$ electronic state at the DZ SCF level of theory we find

$^2B_1$ $3a_1^{1.16}$	$^2A_1$ $3a_1^{1.35}$	$^2B_2$ $3a_1^{0.73}$
110.8°	115.0°	138.4°

These results show indeed that there is a good correlation between methylene bond angle and population of the $3a_1$ orbital. The smallest bond angle is that for the $^2B_1$ state, and it is about 8° greater than observed for singlet CH_2. This difference is nicely explained by the fact that the $^2B_1$ $A\ell CH_2$ angle is about 5° greater than for isolated triplet CH_2, and this is consistent with its $3a_1$ population of 0.73, or 0.27 less than the triplet CH_2 value of unity. Taken together with our previous analogous explanation[17] of several $MnCH_2$ bond angles, it would certainly appear that Walsh-like arguments can be very helpful in explaining the structures of simple organometallic species.

The $^2B_1$ ground state dissociation energy $D_e(A\ell^1-CH_2)$ has been predicted at four levels of theory. The results are 53.0 kcal (DZ SCF), 57.2 kcal (DZ+P SCF), 68.8 kcal (DZ CI), and 77.4 kcal (DZ+P CI). The latter prediction is the most reliable and is about 10 kcal greater than that predicted for the unquestionably single-bond $A\ell CH_3$. Thus the dissociation energies leave open the possibility of a small amount of double bond character for ground state $A\ell CH_2$.

Finally, the predicted dipole moments for $^2B_1$ $A\ell CH_2$ were 0.76 debye (DZ SCF) and 0.74 debye (DZ+P SCF). These dipole moments are only marginally greater than the analogous values for ground state $A\ell CH$ and support the view that the $^2B_1$ ground state of $A\ell CH_2$ is primarily covalent, with a bit of $A\ell^+C^-$ character. The two higher $A\ell CH_2$ states have larger dipole moments, however. The $^2A_1$ state has $\mu = 3.15$ debye at the SCF level with either the DZ or DZ+P basis set. The dipole moments of the energetically higher-lying $^2B_2$ state are 3.01 debye (DZ SCF) and 2.93 debye primarily ionic $A\ell^+C^-$ character for the two excited states of $A\ell CH_2$.

Aℓ ≡ CH Results

In analogy with HCN or HCP, the triply bonded AℓCH should have a collinear equilibrium geometry. Such a species cannot be formally constructed from the CH ground state

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 1\pi \tag{27}$$

since it has only a single unpaired electron. At the DZ SCF level of theory used for all geometry optimizations here, the $^2\Pi$ bond distance is predicted to be 1.1197 Å, in nearly perfect agreement with experiment[35], 1.120 Å.

Turning to the first excited state of CH, the $^4\Sigma^-$ state, we note that it lies only 17.1 kcal[36] above the $^2\Pi$ ground state and arises from the electron configuration

$$1\sigma^2\ 2\sigma^2\ 3\sigma\ 1\pi^2 \tag{28}$$

This configuration has precisely the one unpaired σ orbital and two unpaired π orbitals to make up the desired triple bond.

In $C_{\infty v}$ symmetry the (first excited) $1s^2\ 2s^2\ 2p^6\ 3s\ 3p^2$ configuration (20) of the aluminum atom resolves (maintaining three unpaired electrons) as

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 1\pi^4\ 4\sigma\ 5\sigma\ 2\pi \tag{29}$$

or

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 1\pi^4\ 4\sigma\ 2\pi^2 \tag{30}$$

The latter is properly designed to interact with (28) to form the triply bonded electronic state of AℓCH

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ 5\sigma^2\ 6\sigma^2\ 2\pi^4 \tag{31}$$

In a certain sense (31) is the most "conventional" molecular electronic state of the three organoaluminum complexes considered here, because

(a) it is a closed shell species and (b) the full trivalent nature of Aℓ is utilized.

The predicted linear equilibrium geometry of the triply bonded AℓCH $^1\Sigma^+$ state is seen in Figure 1. The aluminum-carbon distance is 1.668 Å, which is remarkably short and indeed indicative of a genuine Aℓ ≡ C triple bond. For example, one of the shortest known aluminum-carbon distances is 1.86 ± 0.02 Å, for the cubane-like structure[37] $A\ell_4N_4\phi_8$, where the phenyl groups are analogous to the hydrogen atoms in cubane. This structure clearly contains four Aℓ-C single bonds, although most such distances fall in the range 1.9 - 2.0 Å.

A second indication of the Aℓ-C triple bond is the shortness of the adjacent CH bond, namely 1.068 Å. It is well known that CH distances decrease as they are placed adjacent to C - C single, double, and triple bonds. For example, the experimental CH distances[38] in ethane, ethylene, and acetylene are respectively 1.091 Å, 1.086 Å, and 1.058 Å. The predicted CH distance for $^1\Sigma^+$ AℓCH is clearly closest to that found experimentally for acetylene.

The remarkably short Aℓ-C distance in $^1\Sigma^+$ AℓCH makes its electronic structure of particular interest. In this regard, Mulliken populations are given in Table III. These populations immediately stand out with the very first entry showing an Aℓ s population of 4.7, much less than for any of the other molecular electronic states characterized in Table III. This Aℓ 3s population of only 0.66 e^- is indeed indicative of the Aℓ 3s $3p^2$ electron configuration formally required for a triple bond. Confirmation is provided by the Aℓ 3p population of 1.7, the highest recorded in Table III. The reason both 3s and 3p populations fall short of the classical sp^2 picture is the strong polarity $A\ell^{+\delta}(CH)^{-\delta}$ of the $^1\Sigma^+$ state. In the

Mulliken picture, the positive charge δ on aluminum is 0.59 e^-. Actually, the more complete picture of the Mulliken electronic structure of the $^1\Sigma^+$ state is $A\ell^{+0.6}C^{-0.8}H^{+0.2}$. Table III shows in fact that the positive charge on hydrogen is the greatest of any reported here.

The dipole moment of $^1\Sigma^+$ $A\ell CH$ is 6.14 debye at the DZ SCF level of theory and 6.17 debye using the larger DZ+P basis. Such a large dipole moment is, of course, consistent with the substantial Mulliken atomic charges on $A\ell$ and C for the $^1\Sigma^+$ state.

Although the $^1\Sigma^+$ triple $A\ell \equiv C$ bond represents a strong confirmation of qualitative molecular orbital theory, this is not the ground electronic state of $A\ell CH$. That honor goes to the $^3\Sigma^-$ state, arising from the

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ 5\sigma^2\ 6\sigma^2\ 2\pi^2\ 7\sigma^2 \tag{32}$$

Gradient procedures showed that this state is also linear, with the structure shown in Figure 1 and energetics summarized in Table II.

At the DZ+P CI level of theory, the $^3\Sigma^-$ state lies 95.7 kcal below the triply-bonded $^1\Sigma^+$ state. However, this separation is almost certainly too high, since the single configuration SCF treatment is quite poor for the $^1\Sigma^+$ state. A simple, but nevertheless, useful approximate treatment of the importance of higher than doubly excited configurations is Davidson's approximation[39]

$$\Delta E = (1 - C_o^{\,2})\ \Delta E_{SD} \tag{33}$$

In (33), C_o is the coefficient of the Hartree-Fock configuration in the CI wave function, and ΔE_{SD} is the correlation energy due to single and double excitations. Since $C_o = 0.929$ for the $^1\Sigma^+$ state and 0.957 for the $^3\Sigma^+$ state, it is clear that higher excitations are more important for the former.

To be precise, application of (33) reduces the $^3\Sigma^- - {}^1\Sigma^+$ separation to 86.5 kcal.

We must conclude that, although the $^1\Sigma^+$ state represents a triple bond by virtue of its extremely short Aℓ-C equilibrium distance and its electronic structure, this is a very weak bond. Although this result seems contrary to common chemical intuition, we expect such examples to become more common in the future. An experimental example is given by the XeF molecule[40], bound by only 3 kcal, but possessing a bond distance only 20% longer than that found for XeF_2, which contains two more conventional single bonds with average energy greater than 30 kcal. A second example, this one theoretical, is the Cr_2 molecule, with a rather weak Cr-Cr bond, but one which is extremely short[41], indeed suggestive perhaps of a sextuple bond.

The $^3\Sigma^-$ ground state dissociation energy D_e(Aℓ-CH) has been predicted at four levels of theory. The results are 77.9 kcal (DZ SCF), 79.8 kcal (DZ+P SCF), 84.7 kcal (DZ CI), and 87.7 kcal (DZ+P CI). The predictions form a smooth progression and suggest a bond energy ~ 20 kcal greater than that found for the unambiguously single bonded Aℓ-CH_3. This difference would seem to suggest a certain amount of Aℓ-C multiple bond character for $^3\Sigma^-$ AℓCH. This notion is given some support by the predicted $^3\Sigma^-$ structure (Figure 1), which has an Aℓ-C bond distance 0.0039 Å shorter than in AℓCH_3. However, the Mulliken populations (Table III) suggest a $^3\Sigma^-$ electronic structure quite similar to the single bonded AℓCH_3. In fact, there is even less 3s to 3p promotion observed in $^3\Sigma^-$ AℓCH than for AℓCH_3. Thus, while the $^3\Sigma^-$ state does appear to have a somewhat stronger than single Aℓ-C bond, a simple electronic picture confirming this view does not appear at hand.

The predicted dipole moments for $^3\Sigma^-$ AℓCH were 0.37 debye (DZ SCF) and 0.42 debye (DZ+P SCF). Comparison of these μ values with those for the $^1\Sigma^+$ state of AℓCH is interesting. Although the two electronic states have qualitatively similar Mulliken gross atomic charges, the $^3\Sigma^-$ state has a small dipole moment, while the $^1\Sigma^+$ μ value is in excess of six debye. This points out once again the danger inherent in taking Mulliken populations too seriously. From the predicted dipole moments, we conclude that the triply-bonded $^1\Sigma^+$ state is highly polar, while the $^3\Sigma^-$ state is only weakly polar.

After this research was well underway, we noted the appearance of a paper by Pelissier and Malrieu [42] on the AℓN molecule, isoelectronic with AℓCH. Since Pelissier and Malrieu found the $^3\Pi$ state of AℓN to lie 2900 cm^{-1} (8.3 kcal) below the $^3\Sigma^-$ state, it was decided to examine the analogous state of AℓCH. The $^3\Pi$ state arises from the electron configuration

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ 5\sigma^2\ 6\sigma^2\ 2\pi^3\ 7\sigma \qquad (34)$$

and hence might have properties intermediate between those of the triply-bonded $^1\Sigma^+$ state and the $^3\Sigma^-$ ground state.

Table II shows that $^3\Pi$ AℓCH is indeed reasonably low-lying, being placed at 31.0 kcal above the $^3\Sigma^-$ state in the most reliable level of theory, namely DZ+P CI. Nevertheless, it seems clear that the ordering of these two AℓCH states is the opposite of that reported[42] for the isoelectronic AℓN. The $^3\Pi$ AℓCH equilibrium geometry, seen in Fig. 1, confirms the expectation that the structure of (34) should be intermediate between those of electronic states (31) and (32). The predicted dipole moments for the $^3\Pi$ state, namely 3.25 (DZ SCF) and 3.26 (DZ+P SCF) debye, also support this view, that they lie roughly halfway between the triply-bonded ($^1\Sigma^+$) value 6.2 debye and the singly-bonded ($^3\Sigma^-$) result 0.4 debye.

Vibrational Frequencies

The harmonic vibrational frequencies of Table I provide some interesting comparisons. Perhaps most obvious is the fact that $A\ell CH_3$, $A\ell CH_2$, and $A\ell CH$ have respectively 3, 2, and 1 high frequency C-H stretching vibrations. These increase in the order given, a result which may be compared with related series.[38,43] One of the more obvious comparisons is with the family $HO-CH_3$ (methanol), $O = CH_2$ (formaldehyde), and OCH (formyl radical). The observed CH stretching frequencies for the latter molecules are 2840, 2980, and 2980 cm^{-1} (CH_3OH); 2770 and 2840 cm^{-1} (H_2CO), and 2490 cm^{-1} (HCO). After one appreciates from experience that predicted DZ SCF harmonic frequencies (of the type seen in Table I) are typically 10-15% greater than experiment, the general agreement is reasonable. However, the trend for the aluminum molecules is to increasing C-H frequencies across the series $A\ell CH_3$, $A\ell CH_2$, $A\ell CH$, which the opposite trend is observed for the family CH_3OH, CH_2O, CHO.

The family of molecules perhaps most closely related to the single bond $A\ell-CH_3$ species is the methyl halides. Their vibrational spectra have been carefully analyzed[43] and are compared with $A\ell CH_3$ in Table IV. It should be noted that based strictly on atomic masses, the vibrational frequencies of $CH_3A\ell$ should fall between those of CH_3F and $CH_3C\ell$. Although this analogy does not hold strictly, Table IV does seem to indicate a strong similarity between $A\ell CH_3$ and the methyl halides. The principal difference is that the $H_3C-A\ell$ bonding and $C-A\ell$ stretching frequencies are smaller than would be expected from the methyl halides. Both of these results suggest that the $C-A\ell$ bond is weaker than the C-F bond in CH_3F or the $C-C\ell$ bond in $CH_3C\ell$. In fact, the three bond strengths are ~ 75 kcal (this work), 108± 8 kcal, and 83± 2 kcal.

Similar analogies have been constructed in Table V for $^2B_1$ AℓCH$_2$ and $^3\Sigma^-$ AℓCH. The aluminum carbene is compared with formaldehyde (O = CH$_2$) and thioformaldehyde (S = CH$_2$), while the aluminum carbyne is compared with hydrogen cyanide (N $\equiv$ CH) and (P $\equiv$ CH). As expected, the best agreement occurs for the C-H stretching frequencies. The other frequencies for AℓCH$_2$ and AℓCH are notably smaller than the analogous frequencies of the comparison molecules. This, of course, reflects the fact that the Aℓ-C bonds are weaker than the X-C multiple bonds of the comparison molecules. Put another way, the potential energy surfaces of AℓCH$_2$ and AℓCH are much flatter near the minima than those of the comparison molecules. This fact could prove helpful in the identification of hydrocarbon fragments chemisorbed on aluminum metal surfaces.[16-20]

Ionization Potentials

A final comparison of the electronic structures of AℓCH$_3$, AℓCH$_2$, and AℓCH is based on the orbital energies (Koopmans theorem ionization potentials) given in Table VI. There we see first of all a reasonable correlation between aluminum core (1s, 2s, 2p) orbital energies and Mulliken positive charges on the Aℓ atom. That is, the triply-bonded $^1\Sigma^+$ state of AℓCH has by far the greatest ionic character (as noted above, this is only partially revealed by the Mulliken populations), and the greatest Aℓ 1s ionization potential.

The weak Aℓ-C bond in $^1\Sigma^+$ AℓCH is perhaps reflected in the relatively high orbital energy ε for the 2π orbital. However, the other electronic species also display orbital energies in the vicinity of -0.3 hartrees.

An indicator of the relative complexity of the bonding in these four species is the seventh orbital energy, counting from Aℓ 1s. This is the $5a_1$ orbital for AℓCH$_3$ and AℓCH$_2$, and the 4σ orbital for the two states of AℓCH. This orbital is relatively carbon 2s-like for the classical Aℓ-CH$_3$ single bond, where $\varepsilon(5a_1) = -0.9090$. However, this orbital becomes more complicated for AℓCH$_2$ and its ε value is raised. For both states of AℓCH, the 4σ orbital lies much higher (-0.8136 and -0.7979 respectively). As mentioned above, the <u>total</u> carbon 2s population for $^1\Sigma^+$ AℓCH is only 0.66 electrons, requiring the 4σ orbital to be much more strongly mixed.

Concluding Remarks

This paper represents a first step in what is hoped will be a comprehensive study of the interaction between naked aluminum clusters ($A\ell$, $A\ell_2$, $A\ell_3$, $A\ell_4$) and small organic fragments. The key questions answered here concern the ability of atomic aluminum to form multiple bonds to carbon. Although it has been demonstrated that such multiple bonds are indeed predicted for certain electronic states of $A\ell CH_2$ and $A\ell CH$, these multiple bonds are in fact weaker than electronically single bonds of the analogous molecular models. Whether double $A\ell = C$ bonds will be possible for $A\ell_n$ clusters ($n = 2, 3, 4$) remains to be seen. However, the study of such clusters raises the additional possibility of bonding schemes (e.g. bridge, threefold) not possible for the simple prototypes examined here.

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Table. I. Predicted harmonic vibrational frequencies (in cm^{-1}) for the ground electronic states of $A\ell CH_3$, $A\ell CH_2$, and $A\ell CH$.

$A\ell CH_3$		$A\ell CH_2$		$^3\Sigma^-$ $A\ell CH$	
3200	C-H Stretch	3290	C-H Stretch	3350	C-H Stretch
3200		3140		670	Aℓ-C Stretch
3120		1070	$C-H_2$ Scissor	380	Bend
1580	CH_3 Deformation	660	Aℓ-C Bend	380	
1400		640	Aℓ-C Stretch		
1400		630	Aℓ-C Bend		
630	CH_3-Aℓ Bending				
630					
600	C-Aℓ Stretch				

Table II. Total energies for three prototype aluminum-carbon bonds and their respective dissociation limits. The abbreviation TRCI stands for a configuration interaction (CI) including all single and double excitations relative to two reference configurations.

	$A\ell CH_3$	$^2B_1$ $A\ell CH_2$	$^3\Sigma^-$ $A\ell CH$	$^1\Sigma^+$ $A\ell CH$	$^3\Pi$ $A\ell CH$
DZ SCF	-281.47650	-280.85321	-280.23756	-280.02514	-280.16976
DZ TCSCF	-281.48853	--	--	--	--
DZ+P SCF	-281.50030	-280.87471	-280.25457	-280.04734	-280.19126
DZ+P TCSCF	-281.51400	--	--	--	--
DZ CI	-281.61183	-280.97113	-280.33630	-280.18452	-280.28625
DZ TRCI	-281.61416	--	--	--	--
DZ+P CI	-281.70189	-281.04916	-280.39410	-280.24158	-280.34476
DZ+P TRCI	-281.70571	--	--	--	--

	$A\ell + CH_3$	$A\ell + CH_2$	$A\ell + CH$
DZ SCF	-281.40463	-280.76871	-280.11342
DZ+P SCF	-281.42334	-280.78358	-280.12739
DZ CI	--	-280.86154	-280.20135
DZ TRCI	-281.51821	--	--
DZ+P CI	--	-280.92577	-280.25440
DZ+P TRCI	-281.59766	--	--

Table III. Mulliken populations for $A\ell CH_3$, $A\ell CH_2$, and $A\ell CH$ from self-consistent-field wave functions constructed from a double zeta plus polarization basis set.

		$A\ell CH_3$	$A\ell CH_2$	$A\ell CH$	
				$^3\Sigma^-$	$^1\Sigma^+$
Aℓ	s	5.866	5.865	5.888	4.660
	p	6.573	6.574	6.535	7.686
	d	0.014	0.020	0.013	0.068
	total	12.454	12.458	12.436	12.413
C	s	3.401	3.467	3.596	3.363
	p	3.545	3.330	3.081	3.370
	d	0.050	0.052	0.047	0.046
	total	6.996	6.849	6.724	6.779
H	s	0.834	0.830	0.821	0.786
	p	0.016	0.017	0.018	0.022
	total	0.850	0.847	0.840	0.808

Table IV. Comparison between the vibrational frequencies of $A\ell CH_3$ and those of the methyl halides.

	Description	$A\ell$-CH_3	CH_3F	$CH_3C\ell$	CH_3Br
$\nu_4(e)$	C-H Stretch	3200	2980	3040	3060
$\nu_1(a_1)$	C-H Stretch	3120	2960	2970	2970
$\nu_2(a_1)$	CH_3 Deformation	1400	1480	1350	1310
$\nu_5(e)$	CH_3 Deformation	1580	1470	1450	1450
$\nu_6(e)$	HC_3-X Bending	630	1200	1020	950
$\nu_3(a_1)$	C-X Stretch	600	1050	730	610

Table V. Comparison between the vibrational frequencies of $A\ell CH_2$ (ground state) and $A\ell CH$ ($^3\Sigma^-$ ground state) with those of related molecules.

Description	$A\ell CH_2$	$O = CH_2$	$S = CH_2$ [a]
C-H Stretch	3290	2870	3030
	3140	2780	2970
C-X Stretch	1070	1740	--
HCH Bend	660	1500	--
HCH Wag	640	1280	1440
Out-of-Plane Bend	630	1170	--

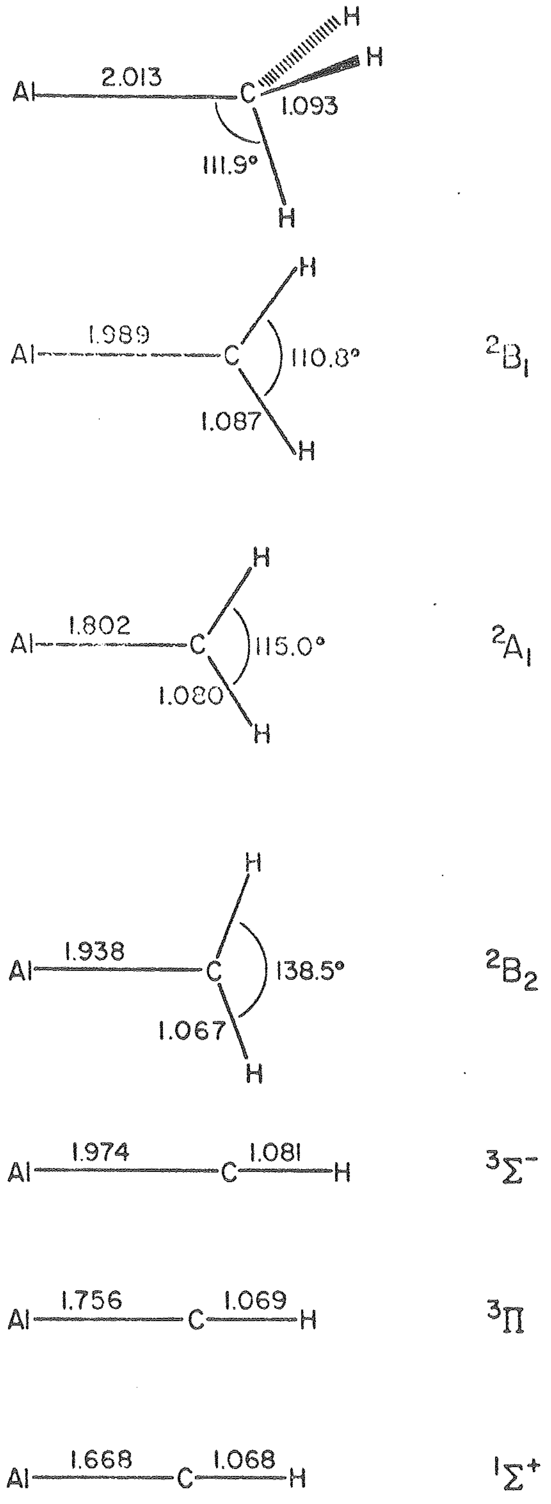
	$A\ell CH$	$N \equiv CH$	$P \equiv CH$
C-H Stretch	3350	3310	3220
C-X Stretch	670	2100	1280
Bend	380	710	670

[a] J. W. C. Johns and W. B. Olson, J. Mol. Spectroscopy **39**, 479(1979).

Table VI. Orbital energies for three organoaluminum molecules at the double zeta plus polarization SCF level of theory.

AℓCH$_3$		AℓCH$_2$		AℓCH			
				$^3\Sigma^-$		$^1\Sigma^+$	
$1a_1$	-58.4704	$1a_1$	-58.4725	1σ	-58.4854	1σ	-58.5260
$2a_1$	-11.1778	$2a_1$	-11.2067	2σ	-11.2270	2σ	-11.2248
$3a_1$	- 4.8840	$3a_1$	- 4.8858	3σ	- 4.8977	3σ	- 4.9435
$1e$	- 3.1929	$1b_2$	- 3.1946	1π	- 3.2061	1π	- 3.2551
	- 3.1929	$1b_1$	- 3.1945		- 3.2061		- 3.2551
$4a_1$	- 3.1916	$4a_1$	- 3.1936	4σ	- 3.2056	4σ	- 3.2553
$5a_1$	- 0.9090	$5a_1$	- 0.8690	5σ	- 0.8136	5σ	- 0.7974
$2e$	- 0.5292	$2b_2$	- 0.5501	6σ	- 0.5513	6σ	- 0.5310
	- 0.5292	$6a_1$	- 0.5012	7σ	- 0.3052	--	--
$6a_1$	- 0.4681	$7a_1$	- 0.2875	2π*	- 0.3820	2π	- 0.2650
$7a_1$	- 0.2770	$2b_1$*	- 0.3603		- 0.3820		- 0.2650

* = Half-occupied orbital


Al
2.013
C
H
H
1.093
111.9°
H
H
Al
1.989
C
110.8°
1.087
H
²B₁
H
Al
1.802
C
115.0°
1.080
H
²A₁
H
Al
1.938
C
138.5°
1.067
H
²B₂
Al
1.974
C
1.081
H
³Σ⁻
Al
1.756
C
1.069
H
³Π
Al
1.668
C
1.068
H
¹Σ⁺

XBL 803-8745

Figure Caption

Figure 1 - Predicted equilibrium geometries of several electronic states of $A\ell CH$, $A\ell CH_2$ and $A\ell CH_3$. Bond distances are in Å.

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