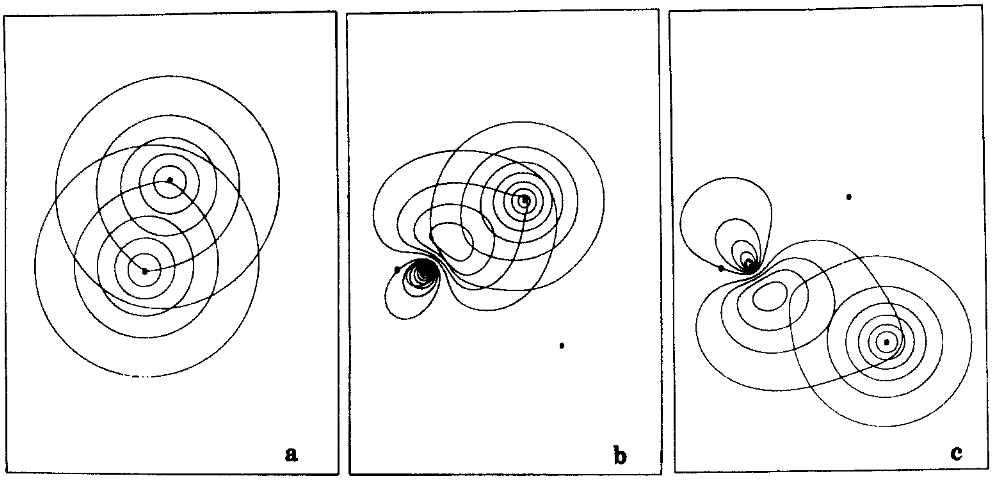

Figure 6. Superimposed contour plots of spin-coupled orbitals: (a) the H-H bond at R = 15 bohr; (b) the first C-H bond at R = 3.0 bohr; (c) the second C-H bond at R = 3.0 bohr.

provided by valence theory, in its proper form, as to which portions of the potential surface should be searched.

Further calculations require larger basis sets and wave functions that take better account of correlation effects over the entire surface. The use of the virtual orbitals generated by spin-coupled theory will allow us to generate a compact set of valence bond structures and, at the same time, to obtain results accurate enough to justify a subsequent dynamical study of the reaction. In particular, we intend to pursue further the approach of H_2 to CH_2 along the direction of one of the nonbonding sp^3-like orbitals.

An MP2 and MCSCF/CI Study of the Aluminum-Acetylene Adducts†

John S. Tse

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9. *Received August 11, 1989*

Abstract: The $\sigma \rightarrow \pi$ conversion of aluminum-acetylene adducts have been examined with ab initio calculations. Contrary to previous studies, the σ-bonded cis adduct was found to be unstable when electron correlations in the valence space were taken into account. Geometry optimization with the MP2 and (CAS)MCSCF methods starting at the cis conformation always converged to a symmetric (π) complex with a $^2B_2$ ground state. A second shallow minimum, separated from the first one by a small potential barrier, was located along the symmetric direction at large Al-C_2H_2 distances by the CASSCF calculations. However, both the barrier and the minimum disappeared when the dynamical correlation effect was included. The $^2A'$ σ-bonded *trans*-aluminoacetylene remained a stable adduct.

1. Introduction

Reactions of unsaturated hydrocarbons with aluminum have a very rich and interesting chemistry. Many organoaluminum complexes can be isolated at low temperature in inert matrices by cocondensation of the metal with excess unsaturated hydrocarbon.[1-6] These adducts are very reactive and useful as catalysts for polymerization reactions.[3-5] Recently, the heat of association of the aluminum atom with simple alkynes and arenes in the gas phase at room temperature has been obtained directly from time-resolved resonance fluorescence experiments.[7] So far, the aluminum adducts of acetylene and ethylene have received the most attention.

There are two possible isomers for the acetylene adduct. The aluminum atom can bond to a single carbon, forming the σ complex, or it can bond to two carbon atoms in the symmetric C_{2v} position. In Al-ethylene, in addition to the symmetric or π conformation, the Al-C bond can either be trans or cis to the unpaired electron on the neighboring carbon atom. Experimental ESR studies suggested that Al-C_2H_2 is a σ adduct whereas Al-C_2H_4 is a symmetric π complex.[1,2,5] The unexpected difference in the mode of chemical bonding between the acetylene and ethylene complexes has generated a great deal of theoretical interest in these systems. Geometry optimizations at the Hartree-Fock level employing double-ζ basis sets show that the σ adducts are the most stable structures for both the acetylene[8,9] and ethylene adducts[10] and the π conformers are the transition

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Table I. Total Energy at the Stationary Points (au)

method	II	III	IV	V	VI[a]	VII	VIII
CASSCF 3-21G	−317.036 42	−317.039 08	−317.036 55	−317.045 83	−317.042 63		
CASSCF CEP-31G(*)	−14.001 49	−13.998 91	−13.990 51	−13.993 30	−13.991 72	−14.003 88	−14.020 61
CASSCF CEP-121G*	−14.030 82	−14.029 98	−14.022 67	−14.025 56	−14.023 67		
FOCI CEP-31G(*)	−14.025 53	−14.027 84	−14.014 98	−14.013 03	−14.011 23	−14.022 02	−14.047 33
FOCI CEP-121G*	−14.063 29	−14.065 78	−14.050 92	−14.046 50	−14.044 01		

[a] Total energy for Al + C_2H_2 calculated at a separation of 20 Å.

states for the [1,2]-shift of the terminal Al atom.

The structure and the stability of the isomers for the reaction of an Al atom with acetylene have been studied in detail at the SCF level.[8,9] In these pioneering investigations, it was found that the Al–C σ bond is surprisingly strong, and both the trans and cis adducts are genuine minima in the potential energy surface. The trans adduct is only marginally more stable than the cis adduct. Moreover, no significant chemical attraction between the acetylene and Al atom was found in the π conformation. This finding is collaborated from the results obtained from a more recent multireference single and double (MRD) CI calculation,[11] which also show that the π interactions between Al and the alkynes are very weak and only a van der Waals complex can be found at large Al–acetylene separation. A similar conclusion was reached in the study on the stability of the adducts from the reaction of an Al atom with ethylene.[10,11]

It is clear that the theoretical results support the experimental findings for the Al–C_2H_2 adduct[1,2] but contradict what has been observed in the Al–C_2H_4 complex.[1,2,5] In view of this discrepancy, the stability of the Al–C_2H_4 π complex was recently reexamined with calculations employing large basis sets and including the effects of electron correlation with full gradient optimization.[12] The results show that although the σ complex is stable in the Hartree–Fock approximation, it is unstable when the effects of electron correlation are incorporated. Geometry optimization starting at the σ complex converges to a symmetric (π) complex with the unpaired electron localized in the Al p_y orbital ($^2B_2$) parallel to the C–C bond. The reason for the instability of the σ adduct is that electron correlation excitations, from the bonding π_{C-C} orbitals to the empty Al 3p orbitals, together with the delocalization of the single electron between the ethylene and Al atom help to enhance the π interactions and favor the symmetric structure. The near-degeneracy of the Al L shell[13] with the π^*_{C-C} orbitals of the alkynes makes the treatment of nondynamical electron correlation essential for these molecules. In light of the unusual findings, it is natural to speculate that similar interactions may also stabilize the π complex in the Al–acetylene system. The focus of this paper is to investigate the influence of electron correlations on the geometries and relative stabilities of the σ and π $^2B_2$ Al–C_2H_2 adducts. In passing, it should be noted that the π complex is not the most stable conformer. In fact, it has been shown previously that the proton-rearranged vinylidene structure is the global minimum.[9]

2. Details of the Calculations

Preliminary exploration of the potential energy surfaces of the σ and π adducts was carried out with the split-valence 3-21G basis set.[14] Further calculations were performed with a compact ab initio effective core potential (CEP),[15] to replace the core electrons of both Al and C atoms in conjunction with the optimized CEP-31G basis set augmented with a set of polarization d functions ($\alpha = 0.25$) on the Al atom (CEP-31G$^{(*)}$).[15,16] Finally, single-point calculations at the optimized stationary points were performed with the triple-ζ CEP-121G* basis set constructed by relaxing the inner contraction of the Gaussians in the CEP-31G$^{(*)}$ and with a set of d functions added on the C atom ($\alpha = 0.6$).[15] To evaluate the accuracy of the pseudopotential approximation, the geometry of the *trans*-Al–C_2H_2 σ adduct was reexamined with the 3-21G basis set augmented with a set of six d orbitals ($\alpha = 0.325$) on the Al atom (3-21G$^{(*)}$).[17]

The structures for the complexes were initially optimized at the UHF level.[18] The structures were then reoptimized taking into account the effects of electron correlation by the Møller–Plesset perturbation correction to the second order (UMP2)[19] and complete active space (CAS) multiconfiguration (MC)SCF.[20] The MCSCF wave functions were designed for the correct description of the zeroth-order correlation only and *not* for describing dynamical correlation. In the MCSCF calculations, the active spaces included all configurations resulting from distributing seven electrons among the eight orbitals of the Al L shell and the π_{C-C} and π^*_{C-C}. This distribution of valence electrons should give an optimum description of the reaction space. The number of spin configurations vary from 588 for the C_{2v} π complex to 1182 for the C_s σ complexes. Geometry optimizations were carried out with analytical gradients. In order to obtain useful binding energy, the contribution from dynamical correlation effects was taken into account through first-order interacting space configuration interactions (FOCI) with the CASSCF wave function as the reference space.[21] The nature of the stationary point was characterized from the evaluation of the force constant matrix. A summary of the geometries of the stationary points located in the present study is depicted in Figures 1 and 2, and the associated total energies are listed in Table I. The calculations were performed with the programs GAUSSIAN86[22] and HONDO7.[23]

3. Results and Discussion

A schematic energy level diagram for the molecular orbitals active in the chemical bonding of Al–C_2H_2 is shown in Figure 3. Both the σ-bonded *cis*-I and *trans*-II structures have a $^2A'$ ground state with the electron configuration ...$1a'^22a'$. In C_{2v} symmetry, the unpaired electron can populate in three different ways. In the $^2B_2$ state III, the singly occupied orbital is the Al $3p_y$ orbital. In the $^2A_1$ state VII, the unpaired electron is located in the Al sp_z hybrid orbital. Finally, the electron may reside in the out-of-plane p_x orbital, giving the $^2B_1$ state. The $^2B_1$ state is expected to be the highest in energy and cannot be obtained via the $^2A'$ state and, therefore, will not be studied in detail here.

The UHF/3-21G-optimized σ-bonded cis (I) and trans (II) Al–C_2H_2 structures are found to be local minima in the potential energy surface, while the π adduct III is the transition state for the [1,2]-shift of the Al atom. This observation is in complete agreement with previous investigations.[8-10] The geometries of the UHF-optimized adducts closely resemble those obtained from ROHF calculations.[8,9] In the σ adducts, the unpaired electron is localized on the uncoordinated C atom in the plane of the

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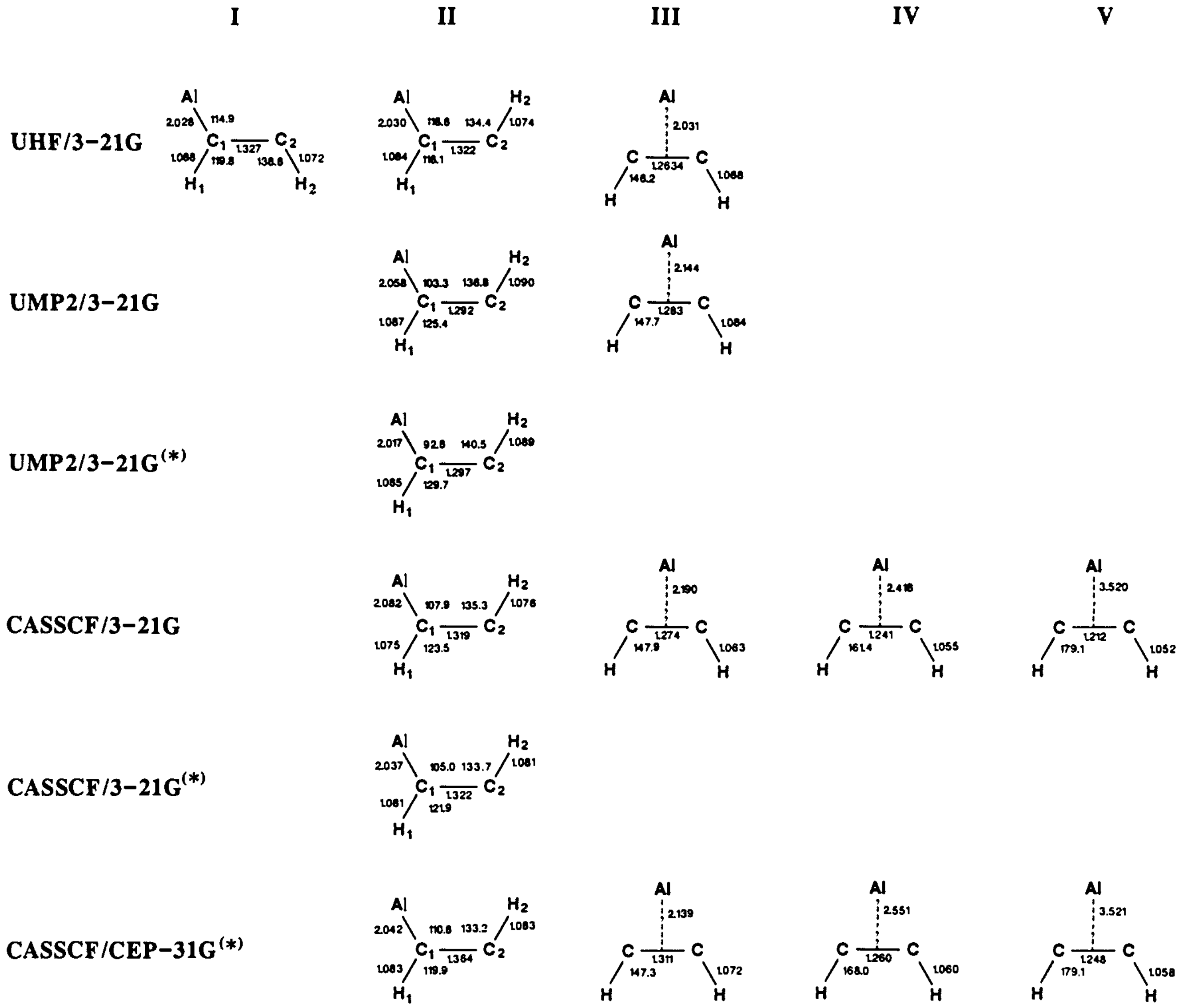
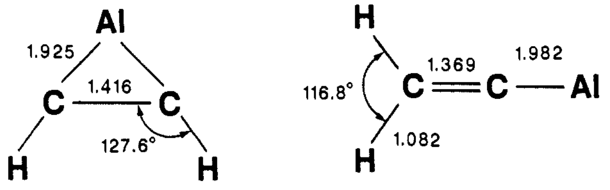


Figure 1. Gradient-optimized geometries for the stationary points located in the Al–C_2H_2 addition reactions.



VII VIII

Figure 2. CASSCF CEP-31G(*)-optimized structures for the $^2A_1$ (VII) and the $^2A'$ Al–vinylidene conformers (VIII).

molecule. Owing to larger repulsion from the bond pair than the lone pair, the H–C–C angles in both complexes, 138.8° in the cis and 134.4° in the trans, are significantly larger than the sp^2-hybridized bond angle. In contrast, the bond angles around the Al-bonded C (C_1) are very close to the ideal 120°. The loss of the triple-bond character in acetylene is also evident in the elongation of the C–C bond to about 1.33 Å. The Al–C distances of 2.03 Å in both σ complexes suggest a normal single bond.[24] In comparison, in the symmetric structure, the Al–C distance is slightly longer with concomitant shortening of the C–C bond to 1.263 Å. The singly occupied molecular orbital in the symmetric structure is delocalized among the Al and the C atoms, with the

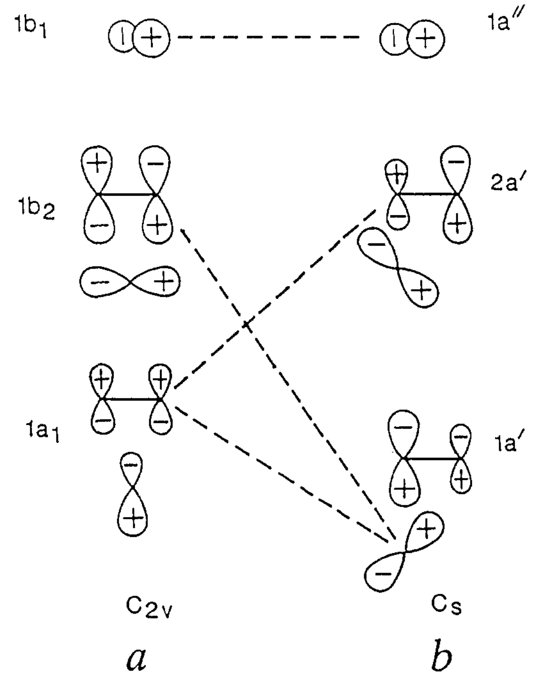


Figure 3. Qualitative molecular orbital diagram illustrating the orbitals active in chemical bonding.

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majority of spin density residing in the Al $3p_y$ orbital parallel to the C–C bond. The UHF/3-21G results are in accord with the analysis of the ESR spectra, which strongly suggested the formation of σ-bonded structures. Experimentally, when Al is cocondensed with acetylene in neon matrices at low temperature, the ESR spectrum is consistent with a σ-bonded trans structure.[1,2] Photoirradiation of matrices containing the $Al-C_2H_2$ adduct changed the ESR spectrum drastically. Although agreement between the experimental and the simulated ESR spectrum was unsatisfactorily, nevertheless, the new species was tentatively assigned to a metastable cis conformer of the σ-bonded adduct.[2]

The ground-state UHF wave functions of the σ adducts are heavily contaminated with spin states of higher multiplicities,[25] suggesting that a single-determinant Hartree–Fock approximation may not be sufficient in describing the electronic structure of the molecules. To obtain better geometries and energetics, the stationary-point structures were then reoptimized with the UHF results as the starting point and including the effects of electron correlations. The UMP2- and CASSCF-optimized structures for the trans adduct II are comparable to each other and in qualitative agreement with the UHF results. Bond lengths obtained from effective core potential calculations are in general longer than those from the 3-21G basis set.[15] As expected, the uncorrelated C–H bonds are shorter in the MCSCF than in the UMP2 structure.[26] It is interesting to note that both the Al–C and C–C bonds in the UMP2 structure are shorter than in the CASSCF-optimized structure. This effect has also been noted in the study of the Al_2 dimer where the interatomic separation decreases with the inclusion of electron correlation.[27,28] The excitations from the filled molecular orbitals to the low-lying unoccupied Al 3p orbitals help to strengthen the chemical bonds. Calculations with the 3-21G$^{(*)}$ basis sets have little effect on the structures. The most noticeable difference is in the ∠Al–C–C bond angle, which reduces from the 3-21G value of 107.9° to 105.0° in the CASSCF calculations. The distortion is even more significant in the MP2 structure where the angle changed from 103.3° to 92.6°. Finally, the CEP-31G$^{(*)}$ structural parameters are very similar to those obtained from the 3-21G$^{(*)}$ calculations, and this basis set has been used in the calculations described below.

As expected, the 3-21G basis set failed to provide reliable absolute energy. CASSCF calculations with ECP gave slightly better results. The MCSCF CEP-31G$^{(*)}$ and CEP-121G* binding energies are −6.13 and −4.49 kcal/mol, respectively. An even better estimate is the FOCI/CEP-31G$^{(*)}$ value of −8.97 kcal/mol, which increases to −12.29 kcal/mol with the CEP-121G* basis set. The large difference between the CASSCF and FOCI results shows a substantial contribution from dynamical correlation effects in binding. The experimental zero-point energy corrected binding energy for $Al-C_2H_2$ is found to be >13 kcal/mol.[17] The CASSCF/ECP-31G$^{(*)}$ harmonic vibrational frequencies compare very well with the RHF results,[9] except that the vibrations of the bonds correlated in the CASSCF calculations are consistently lower than the RHF values. This effect can be attributed to an exaggeration of bond lengths due to an overemphasis on the left–right correlation by the MCSCF method.[26]

Incorporation of electron correlation alters stability of the cis conformer drastically. Geometry optimization, starting at the UHF cis structure with the UMP2 procedure, converges into the symmetric structure III. A similar result was also obtained with CASSCF calculations, even when the initial geometry and Hessian matrix were taken from the ROHF-optimized cis structure. Calculations with the slightly larger CEP-31G$^{(*)}$ basis set yield the same results. The driving force for the migration of the Al atom from the terminal to the symmetric position is primarily due to excitations of the unpaired electron localized on the β-C into the neighboring empty and spatially diffuse Al 3p 3a′ orbital ($\langle r \rangle_{3p}$ = 1.82 Å), which enhances the lateral Al–C interactions. Since this kind of excitation is neglected in the Hartree–Fock model, the cis structure becomes a local minimum. On the other hand, the anti arrangement of the singly occupied molecular orbital with respect to the Al empty orbitals in the trans adduct precludes any significant enhancement in the overlaps. Consequently, no substantial destabilization in favor of the symmetric structure is expected, even when electron correlations are considered and the trans adduct remains stable.

Table II. CASSCF CEP-31G(*) Harmonic Vibrational Frequencies (cm^{-1})[a]

II		III		IV	
3360	$\nu_{C_2-H_2}$	3493	ν^s_{C-H}	3685	ν^s_{C-H}
3314	$\nu_{C_1-H_1}$	3432	ν^a_{C-H}	3584	ν^a_{C-H}
1539	ν_{C-C}	1735	ν_{C-C}	1923	ν_{C-C}
1202	$\delta_{Al-C_1-H_1}$	801	δ^s_{C-C-H}	716	$\tau_{H-C-C-H}$
949	$\tau_{H-C-C-H}$	760	δ^a_{C-C-H}	599	δ^a_{C-C-H}
926	$\tau_{H-C-C-H}$	654	$\tau_{H-C-C-H}$	583	δ^a_{C-C-H}
551	ν_{Al-C}	603	$\tau_{H-C-C-H}$	574	$\tau_{H-C-C-H}$
468	$\tau_{Al-C_1-C_2-H_2}$	404	$\nu_{Al\cdots HCCH}$	221	$\tau_{Al\cdots HCCH}$
158	$\delta_{Al-C_1-C_2}$	179	$\tau_{Al\cdots HCCH}$	226i	$\nu_{Al\cdots HCCH}$

[a] ν, δ, and τ represent stretching, bending, and torsional vibrations, respectively.

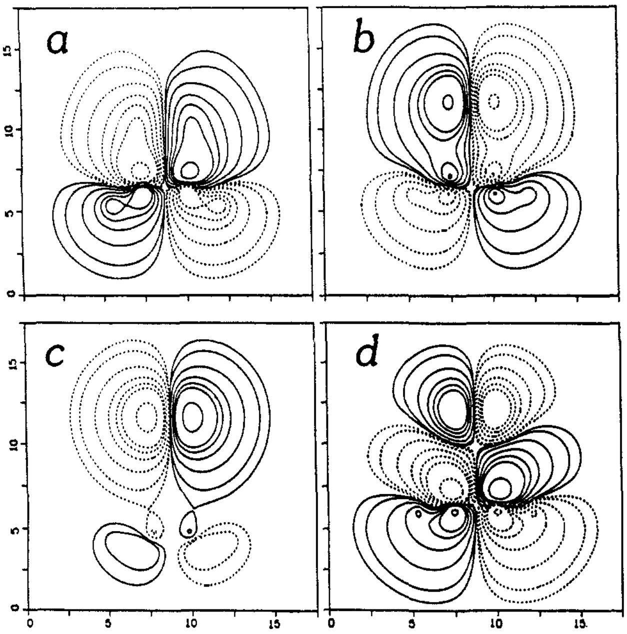

Figure 4. Contour diagram for the SOMO CI wave functions of the C_{2v} complexes: (a) first minimum; (b) transition state; (c) second minimum; (d) the second state at the transition state.

The C_{2v} structure III is identified to be a local minimum through the evaluation of the harmonic vibration frequencies (Table II). The C–C stretching frequency of 1735 cm^{-1} in III is closer to that of free C_2H_4[26] and substantially higher than that in the trans adduct (II). However, the $Al\cdots C_2H_2$ symmetric stretch (404 cm^{-1}) is lower than the Al–C stretch (551 cm^{-1}) in II. Once again, there is little difference between the UMP2 and CASSCF structural parameters. The C–C bond lengths in the symmetric structures are shorter than those in the corresponding trans isomer by an average of 0.05 Å. All the observations point to the C–C bond strength being halfway between a double and a triple bond. Furthermore, the H–C–C angles are predicted to tilt away from the Al atom and deviate significantly from linearity, indicating substantial rehybridization at the C atoms. The Al–C bond remains fairly strong as the distance is only 0.1 Å longer than that in the trans isomer. In fact, the sum of the bond indices for the two Al–C bonds of 0.841 is greater than that calculated for the σ-bonded trans adduct of 0.747. An analysis of the MCSCF natural orbitals reveals that the valence electrons are very active. Apart from the usual left–right $\pi_{C-C}{}^2 \rightarrow \pi^*_{C-C}{}^2$ correlation, the ionic configuration $1b_2(Al\ 3p_y) \rightarrow 2b_2(\pi^*_{C-C})$ $(Al-C_2H_2 \rightarrow Al^+C_2H_2^-)$ also makes a significant contribution. The occupancy

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of the antibonding $2b_2$ natural orbital is more than 0.04, and those in the Al $3p_x$ and $3p_z$ orbitals are 0.7 and 0.3, respectively. The wave function for the singly occupied MCSCF natural orbital is plotted in Figure 4a. As shown in the diagram, the bonding scheme is consistent with the conventional Dewar–Chatt–Duncanson description for metal π complexes.[29,30] Collaborative interactions between the filled π_{C-C} with the empty Al $3p_x$,$3p_z$ and the delocalization of the unpaired electron in the Al $3p_y$ and the π^*_{C-C} orbital strengthen the symmetric structure. Orbital analysis supports this bonding picture. The gross populations of the formally empty Al $3p_{x,y}$ orbitals are 0.12 and 0.29, respectively, while the population of the electron-donating Al $3p_y$ orbital is 0.47 and the resulting total charge on the acetylene is −0.15e.

The binding energy of the symmetric structure is comparable to that of the trans adduct. At the CASSCF level, the calculated binding energies are, −4.51 and −3.96 kcal/mol with the CEP-31G$^{(*)}$ and CEP-121G* basis sets, respectively. Inclusion of dynamical correlation increases the CEP-31G$^{(*)}$ binding energy to −10.42 kcal/mol and the CEP-121G* binding energy to −13.66 kcal/mol. The present results are in complete agreement with the recent findings on the analogous Al–C_2H_4 adducts.[12] In the recent work,[12] it was shown that the symmetric adduct is stable only when the effects of electron correlation and hybridization are properly considered. More importantly, the instability of the σ-bonded cis adduct is independent of the quality of the basis sets employed in the calculations. For the Al–C_2H_4 molecule, calculations with 3-21G and the triple-ζ MC-311G* basis sets yield essentially identical results. We conclude that a proper treatment of electron correlation in the Al 3s,3p valence space and the near-degeneracy with the alkyne π orbitals is mandatory for a correct description of the bonding between the Al atom and olefins.

The C_{2v} structure obtained here differs from those previously reported. In an earlier study,[11] it was shown that the potential energy curve along the symmetric direction is repulsive at small separation. A shallow minimum was located at an Al–C_2H_2 separation of 3.147 Å in which the C_2H_2 molecule is only slightly distorted from the free state. The small calculated binding energy of −2.44 kcal/mol suggests the interactions are van der Waals in nature. The present study, however, shows that a strong and stable symmetric Al–C_2H_2 adduct can be formed. In previous calculations, global geometry optimization was not performed. The geometry of the C_2H_2 molecule was fixed during optimization of the Al–C_2H_2 distance. As already mentioned, the C atoms have to rehybridize continuously in order to maintain maximal overlap with the Al atom. This procedure certainly will not give the optimal energy and structure at each separation.

It was of some interest to search for the van der Waals minimum predicted previously. To this end, the potential energy surface for the symmetric adducts was examined as a function of the Al and C_2H_2 distance with CASSCF/3-21G calculations. The geometry of the adduct was fully optimized at each separation. The results of the calculations are summarized in Figure 5. A salient feature of the potential energy curve is the appearance of two minima separated by a small barrier. The first minimum at 2.189 Å corresponds to π-adduct III already discussed. A second shallow minimum V occurs at 3.520 Å. The two energy minima are separated by a potential barrier IV maximized at 2.418 Å. Further lengthening of the Al–C_2H_2 interaction separation from the second minimum leads to a smooth dissociation into a ground-state Al(^2P) atom and the C_2H_2($^1\Sigma_g^+$) fragment. The CASSCF/3-21G total energies of the adducts are overestimated at large Al–C_2H_2 distances, undoubtedly due to basis set superposition errors (BSSE). BSSE have been found to be important for similar metal–alkyne systems.[31] The structures of the stationary points were then reoptimized with the larger CEP-31G$^{(*)}$ basis sets. The calculations with the larger basis sets (CEP-31G$^{(*)}$ and CEP-121G*) validate the findings but reverse the stability of the two stable adducts. The CASSCF/CEP-121G* energy difference between the two minima is 2.77 kcal/mol.

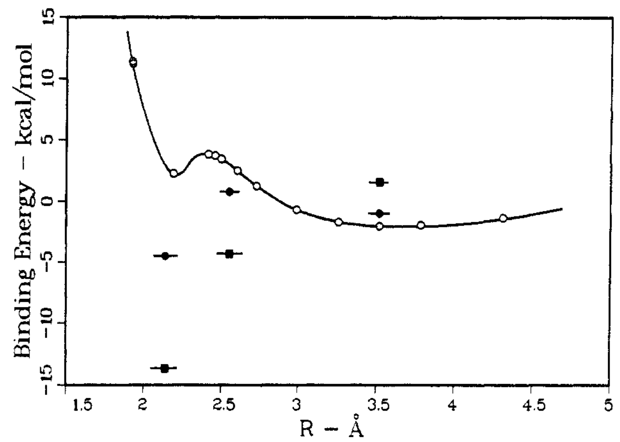

Figure 5. Potential energy surface along the symmetric direction: (○) CASSCF/3-21G; (●) CASSCF/CEP-31G$^{(*)}$; (■) FOCI/CEP-121G*. The solid curve is a guide to the eye.

The geometry of the second minimum V agrees very well with the van der Waals complex reported previously.[11] The C_2H_2 fragment is slightly perturbed by the Al atom. At the CASSCF/CEP-31G$^{(*)}$ level, the C–C and C–H bonds are only 0.001 and 0.0005 Å longer than in the free molecule. As shown in the contour diagram of the singly occupied molecular orbital (Figure 4c), the unpaired electron resides predominantly in the Al $3p_y$ orbital. The interactions of the Al atom with the acetylene molecule are minimal. The binding energy of this complex is about 1 kcal/mol (see Table I), which is lower than the earlier reported MRDCI value of 2.44 kcal/mol.

The potential barrier was not observed in the earlier study[11] of the Al–C_2H_2 potential energy curve. It is caused by the avoided crossing of the low-lying covalent and ionic states of $^2B_2$ symmetry. This interaction is illustrated from a study of the FOCI wave function of the two low-lying $^2B_2$ states. In the ground state, there is a strong admixture of the HF determinant (0.873) and the $1b_2 \rightarrow 2b_2$ (−0.323) (Al $3p_y \rightarrow \pi^*_{C-C}$) configurations in the wave function. The CI coefficients for the respective configurations are −0.308 and −0.820 in the second state. The structure at the energy maximum corresponds to the transition state of the dissociating motion with an imaginary frequency of 226*i* cm^{-1} (Table II). In general, the vibrations in IV are closer to those of the free molecule[32] than those of the π complex. In particular, the C–C stretch has increased by almost 200 cm^{-1} in III to 1923 cm^{-1} in IV. The singly occupied MCSCF natural orbital of the ground and first excited states at the saddle point are displayed in Figure 4. In comparison with the π adduct (Figure 4a), the electron density around the Al atom is more diffuse and the Al–C_2H_2 interactions are evidently much weaker (Figure 4b). The excited wave function is predominantly π^*_{C-C} and Al–C_2H_2 antibonding. The large concentration of charge density on C_2H_2 clearly identifies the strong ionic $Al^+C_2H_2^-$ character.

At the CASSCF level, the CEP-31G$^{(*)}$ and CEP-121G* energies of the saddle point are higher than the first π complex by 4.23 and 4.59 kcal/mol, respectively. It is interesting to note that the inclusion of dynamical correlation through FOCI calculations lowers the energy of the barrier below that of the second minimum. Although no new geometry search for the stationary points was performed, it is likely that both the potential barrier and the second minimum may disappear at the CI level.

In many respects, the bonding in the Al–alkyne adducts is very similar to that of the transition-metal Ni–[31b,33] and those of the main-group Li–, Be–, and Mg–alkyne adducts.[33,34] In the case

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of Ni, the binding energy for the association reaction is more than compensated for the excitation from the ground $^3F(d^8s^2)$ state to the excited ^1D state. Therefore, the nickel atom can be s–d hybridized and interact more efficiently with the π system of the alkynes to form stable complexes in the classical Dewar–Chatt–Duncanson fashion. The resemblance of the geometries of the nickel adducts to that of the aluminum analogue is striking. In the $^1A_1$ NiC_2H_2, the C_2H_2 moiety is almost halfway distorted into a C_2H_4. The C–C bond of 1.262 Å and ∠H–C–C of 148° are very close to those observed in the present study. The bonding in the Al–acetylene system also parallels that in Li–acetylene.[34] In the latter case, UHF/3-21G calculations[10] failed to locate the symmetric structure as well. In contrast, UMP2/6-31G* calculations[34] show that both the π-bonded and the trans σ-bonded structures are stable. A similar observation has also been made in a study of the C_{2v} interactions of Be and Mg atoms with acetylene and ethylene molecules.[35] It was shown that distortion of the hydrocarbons is important for the interactions. Earlier calculations with fixed hydrocarbon geometries did not predict any binding for the π complex.[10,36] More significantly, an ionic structure, similar to that discussed above, was found for the reactions of ^1S Be and Mg at small metal–alkyne distance. The ionic structure is separated from a second stable covalent structure by an activation barrier.

Formation of the C_{2v} $^2A_1$ complex (VII) from Al and acetylene along the symmetric direction requires very large activation energy. A minimum energy structure is located at a relatively short Al–acetylene separation. The three-membered ring structure of the $^2A_1$ state consists of two strong Al–C bonds (Figure 2). The CASSCF CEP-31G$^{(*)}$-optimized Al–C distance of 1.925 Å falls between a single and double Al–C bond.[24] The ∠C–C–H angle of 127.6° clearly shows the carbon atoms have completely rehybridized to sp^2. The C–C bond length of 1.416 Å is typical of a partial double bond. The MCSCF wave function of the $^2A_1$ state is found to be a strong admixture of several excited configurations. The CI coefficient of the Hartree–Fock configuration is 0.80, which amounts to only 64% of the MC wave function. Mulliken population analysis shows that the $^2A_1$ structure is much less ionic than the $^2B_2$ state and the net spin population is mainly localized on the Al atom. The energy of the $^2A_1$ state is expected to be nearly degenerate with the $^2B_2$ state. The CASSCF CEP-31G$^{(*)}$ energy is 3.12 kcal/mol below that of the $^2B_2$ state (Table II); however, a reverse order is observed from the FOCI calculations.

In agreement with previous findings, the global minimum of the Al–ethylene conformers is the vinylidene structure (VIII). The binding energy of −22.7 kcal/mol obtained from the FOCI/CEP-31G$^{(*)}$ calculation is consistent with the previously estimated value of −28 kcal/mol.[9] Apart from the expected lengthening of the correlated Al–C and C–C bonds, the MCSCF-optimized structure shown in Figure 2 is comparable with those obtained from earlier SCF results.[9]

4. Conclusion

The results presented here demonstrate the importance of near-degeneracy effects in the bonding of aluminum with alkynes. The σ-bonded cis adduct is found to be unstable when electron correlations in the valence space are properly accounted for. More importantly, the symmetric π-bonded structure, which was predicted as a transition state for the [1,2]-shift of the terminal Al atom in previous UHF and RHF calculations,[8,9] is identified as a local minimum. Large basis set calculations at the CASSCF/FOCI level give the binding energy of the symmetric adduct as −13.66 kcal/mol, which is comparable to that of the trans adduct. The driving force for the cis → π (C_{2v}) rearrangement is mainly due to the favorable lateral interactions of the unpaired electron located in the vicinity of the Al atom. The σ-bonded trans adduct is stable with the inclusion of electron correlation effects. Experimentally, the trans adduct was identified in the reaction of Al with C_2H_2 in a rare-gas matrix under cryogenic conditions. The cis adduct was believed to be the product of photoirradiation of the trans isomer. The symmetric $^2A_1$ and $^2B_2$ adducts have not been observed experimentally. The $^2A_1$ adduct is not expected to form under normal conditions due to the high activation barrier. Further ESR experiments with different matrices may be required in order to confirm the predicted existence of the $^2B_2$ π complex. Since the energy difference between the isomers is very small, the interactions with the supporting matrix may influence the stability of the isomers. The features of the potential energy surface for the addition reaction of a main-group metal atom with an unsaturated hydrocarbon share many similarities. The existence of two minima along the symmetric C_{2v} direction due to avoided crossing of the ionic and covalent states appears to be a general phenomenon.[33-35] In passing, it is worth commenting that although no diffuse function was used in the present study, previous calculations on similar systems[35] have shown that the present basis set is adequate to give a qualitative description of the bonding.

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