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Acetylene, Vinylidene, and the Vinyl Cation in Ground and Excited States*

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Ab initio calculations using the improved virtual orbital formalism are reported for acetylene, vinylidene, and the vinyl cation, $C_2H_3^+$, in classical and bridged geometries. Electronic transition energies and equilibrium geometries for ground and lower lying electronically excited states have been calculated. A modified Walsh diagram for acetylene and simple molecular orbital considerations explain excited state structures and energy orderings. While acetylene in the ground state is much more stable than vinylidene, the energies of several corresponding excited states are comparable. The stabilities of bridged and classical structures of the vinyl cation are very similar in the ground state, but in the various excited states either structure can predominate. The proton affinity of acetylene in the ground state should be appreciably lower than in excited states.

INTRODUCTION

First invoked in the electrophilic reactions of alkynes, vinyl cations are now common reactive intermediates.¹ Since the proton affinity of acetylene is about 10 kcal/mol less than that of ethylene, the parent vinyl cation, $C_2H_3^+$, is extremely reactive and can only be observed experimentally in the gas phase.² However, many details of the ground state have been revealed by a number of theoretical investigations.³⁻⁹

In relation to the photochemistry of alkynes we have now studied new aspects; the protonation of acetylene in the lowestlying excited singlet and

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triplet states. We also reconsider the problem of the excited states of acetylene itself.

Only a few carbocations with triplet ground states have been reported. These include $C_5H_5^+$ and its relatives,¹⁰ C_2H^+ ,^{9,11} and lithiated carbenium ions like CLi_3^+ .¹² Prior studies of triplet and singlet excited states of carbocations also are rare. The triplet methyl cation ($^3A''$), for example, is calculated to lie about 88 kcal/mol above the singlet ground state in energy and to have a non-planar geometry with C_s symmetry.¹² Excited states of the vinyl cation are also likely to exhibit interesting features.

In this respect, knowledge of the ground and excited states of the corresponding deprotonated species, acetylene ($HC\equiv CH$) and its isomer, vinylidene ($H_2C=C$), is desirable. Both $C_2H_3^+$ and C_2H_2 are isoelectronic, but the vinyl cation possesses an additional C—H bond. The excited states of acetylene are the subject of an extensive literature, both experimental and theoretical.^{18-21*} Non-linear forms are favored, and *cis*- and *trans*-isomers have been calculated. While linear excited states have been considered to connect these two forms, we will show in the present work that other transition structures are lower in energy. With the exception of the triplet, excited states of vinylidene have not been investigated extensively before.²²

A further point deals with energetic ordering of the molecular orbitals and the related sequence of the various excited states.²¹ Heretofore, this sequence could not be clarified by means of simple MO theory. We will show that a modified Walsh diagram as well as an additional correction for the nearly degenerate MO's allows a complete understanding of the sequence of both singlet and triplet states.

CALCULATIONAL METHODS

The ab initio SCF calculations employed at the Gaussian lobe 4-31G basis set¹⁴ augmented by diffuse (s,p) functions (exponent 0.05) at the carbon atoms. These were included so that Rydberg states could be taken into account. The exponent chosen is similar in magnitude to that of the 4-31+G basis set, designed for calculations on carbanions, which also have occupied orbitals with diffuse character.¹⁵ The ground and lowest electronically excited singlet and triplet state geometries were calculated for both *trans*- and *cis*-conformations of planar C_2H_2 .

In order to examine excited states, truncated CI treatments were carried out within the molecular orbital framework. These were designed to provide balanced approaches to the ground and excited states as far as is possible within Koopman's approximation.¹⁶ The singly excited configurations used have common occupied MO's from which excitations, carried out conveniently within the formalism of improved virtual orbitals, are performed.¹⁷ Vertical as well as non-vertical electronic transitions are expected to be given more accurately by this procedure than by some alternative treatments which tend to favour the ground state.¹⁸

RESULTS AND DISCUSSION

Acetylene Ground and Excited States

In the most detailed earlier study, So, Wetmore, and Schaefer²¹ found different energetic orderings of the excited singlet ($^1A_u < ^1A_2 < ^1B_2 < ^1B_u$) and triplet ($^3B_2 < ^3B_u < ^3A_u < ^3A_2$) states of acetylene, but could provide no qualitative rationalization in terms of Walsh diagram arguments.

* See also O. Nomura and S. Iwata, *J. Chem. Phys.* **74** (1981) 6830 (added in proof)

TABLE I
Orbital Energies (a. u.) of Acetylene in its Ground State Geometry

Doubly occupied (valence) and vacant SCF orbitals ground state	Improved virtual orbitals when $\pi_u(x)$ is singly occupied	
	singlet	triplet
— 1.04697 σ_g		
— 0.76684 σ_u		
— 0.68747 σ_g		
— 0.41590 π_u		
0.08887 $\sigma_u R$	— 0.17103 $\pi_g(y)$	— 0.22303 $\pi_g(x)$
0.09402 $\sigma_g R$	— 0.08962 $\sigma_g R$	— 0.19302 $\pi_g(y)$
0.12398 $\pi_g R$	— 0.08027 $\sigma_u R$	— 0.10205 $\sigma_g R$
	— 0.05565 $\pi_g(x) R$	— 0.09129 $\sigma_u R$

R: Rydberg orbitals

To provide a better overview into the nature of the problem, we first consider vertical excitations of acetylene. Table 1 gives the orbital energies for the acetylene ground state. Next, the vacant orbitals were calculated again under the conditions that $\pi_u(x)$ was singly occupied. By removing appropriate terms from the Fock operator, the energies of the improved virtual orbitals corresponding to singlet and triplet states were obtained. These not only differ from one another in their ordering, but also from the original ordering of the unoccupied MO's in acetylene. This original ordering may thus be inappropriate not only for drawing Walsh diagrams but also for estimating excitation energies. The improved virtual orbitals should be used instead for both these purposes.

For example, vertical electronic transition energies can easily be evaluated as differences between doubly occupied and improved virtual orbitals. The Rydberg states, easily identified by orbitals with large coefficients for the diffuse basis functions are of further interest. Table 1 shows that the Rydberg character of an orbital sometimes depends on whether this orbital is empty or singly occupied. Besides vertical transitions the nonvertical electronic transitions are of specific importance in photochemistry. The orbital analysis of the vertical transitions can provide a very useful qualitative description of equilibrium geometries in excited states and facilitates quantitative investigations.

The original Walsh diagram¹⁹ for *cis* (C_{2v}) and *trans* (C_{2h}) HAAH systems provided a convincing rationalization for the strongly non-linear preferences of the lowest excited singlet and triplet states of acetylene.¹⁹⁻²¹ In Table 2, the correlation diagram connecting these forms is extended to include a half-bent (C_s) intermediate structure.

TABLE II

Correlation Scheme for Orbital Symmetries of HAAH Molecules in *cis* (C_{2v}), Linear ($D_{\infty h}$), Half Bent (C_s) and *trans* (C_{2h}) Arrangements

C_{2v} <i>cis</i>	$D_{\infty h}$ ^a	C_s ^b	C_{2h} <i>trans</i>
a_1	σ_g	a'	a_g
b_2	σ_u	a'	b_u
a_1	π_u	a'	b_u
b_1	π_u	a''	a_u
a_2	π_g	a''	b_g
b_2	π_g	a'	a_g

^a Linear transition state ($D_{\infty h}$); ^b Half bent-half linear transition state (C_s).

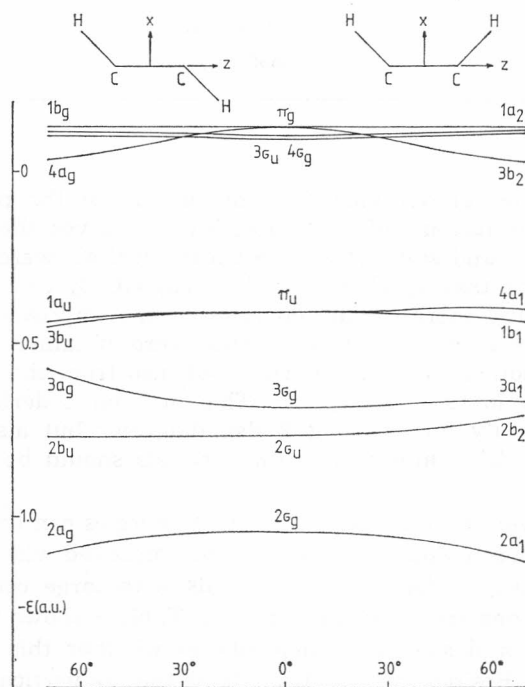


Figure 1. Modified Walsh diagram for linear and *cis* and *trans* bent acetylene, calculated at 30° intervals. The axis convention is shown.

However, the original Walsh diagram¹⁹ has features which are not confirmed by exact calculations (shown in Figure 1). Thus, *cis* and *trans* geometrical distortions do not always lead to similar raisings and lowerings. Other connections also are indicated: In the original diagram for *cis* and *trans* conformations, the orbitals $4a_1-3b_u$ and $1b_1-1a_u$ are connected. In Figure 1 alternative pairings are suggested: $4a_1-1a_u$ and $1b_1-3b_u$. This reflects the ordering in Table 3 better, and leads to the correct prediction that the singlet

1A_u (*trans*) state is favored over 1A_2 (*cis*). The same applies to the triplet A states. Likewise, the 3B_2 (*cis*) state is favored over 3B_u (*trans*); the singlet B states are ordered similarly.²⁰

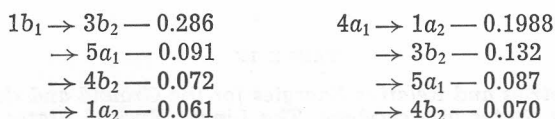
TABLE III

Valence Orbital Energies (a. u.) for the Ground and Excited States of Acetylene. The Last two Orbitals of the Excited States are Singly Occupied; Improved Virtual Orbitals are Utilized for the Highest Energy Orbital

${}^1\Sigma_g^+$	1A_2	1A_u	3B_2	3B_u
-1.047 σ_g	-1.025 a_1	-1.029 a_g	-1.038 a_1	-1.036 a_g
-0.767 σ_u	-0.771 b_2	-0.784 b_u	-0.763 b_2	-0.781 b_u
-0.687 σ_g	-0.661 a_1	-0.623 a_g	-0.656 a_1	-0.632 a_g
-0.416 π_u	-0.389 a_1	-0.412 b_u	-0.398 b_1	-0.398 a_u
	-0.394 b_1	-0.392 a_u	-0.390 a_1	-0.413 b_u
	-0.286 b_2	-0.326 a_g	-0.369 b_2	-0.352 a_g

Furthermore the splitting of the two π_u orbitals due to symmetry reduction is so small that the usually applied aufbau principle fails for these closely spaced orbitals. In other words, neither the original¹⁹ nor the new Walsh diagram (Figure 1) allows a reliable qualitative decision to be made concerning the preferred occupancy.

For example, consider various excitations from $1b_1$ or from $4a_1$. The energetic orderings of the resulting singly occupied orbitals are quite different:



The lowest excited singlet state with the *cis* conformation (1A_2) and the lowest excited triplet state with the *trans* conformation (3B_u) both are derived from excitations ($1b_1 \rightarrow 3b_2$ and $3b_u \rightarrow 4a_g$, respectively) which do not originate from the highest occupied orbital (see Figure 1). The valence orbital energies are represented in Table 3 for the ground state as well as for the lowest singlet and triplet states in their calculated local minima.

Thus we have arrived at the following situation: While the Walsh diagram is able to predict the preference for *cis* or *trans* conformations of a given state, it is incapable of ordering the different states among each other. The Walsh diagram predictions are:



However, even though the *cis-trans* energy differences are much smaller than those between different states, e. g., between A_2 and B_2 , these cannot be ordered readily.

The energetic sequence of the 1A_2 and 1B_2 as well as the 3A_2 and 3B_2 states can easily be predicted on the basis of the present results. The A_2 and B_2 states involve excitations, $4a_1 \rightarrow 1a_2$ and $4a_1 \rightarrow 3b_2$, respectively. Because of

the close energetic relationships shown in Figure 1, the former is essentially a $\pi_u(x) \rightarrow \pi_g(y)$ excitation, while the latter involves $\pi_u(x) \rightarrow \pi_g(x)$. Singlet and triplet excitation energies to the same configuration are given by

$$\Delta E \begin{pmatrix} S \\ T \end{pmatrix} = \varepsilon_k - \varepsilon_i - J_{ik} + \begin{pmatrix} 2K_{ik} \\ O \end{pmatrix}.$$

When wellknown relationships are employed,

$$J_{xx} = K_{xx} \quad \text{and} \quad J_{xx} = J_{xy} + 2K_{xy},$$

one obtains as an approximation for ΔE :

	$\pi_u(x) \rightarrow \pi_g(x)$	$\pi_u(x) \rightarrow \pi_g(y)$
S	+ J_{xx}	- $J_{xy} + 2K_{xy}$
T	- J_{xx}	- J_{xy}

(The difference $\varepsilon_k - \varepsilon_i$ is neglected due to the essentially degenerate character of the $1a_2$ and $3b_2$ orbitals.)

Because $J_{xx} > J_{xy}$, it follows that ${}^3B_2 < {}^3A_2$; since $J_{xx} > -J_{xy} + 2K_{xy}$, ${}^1A_2 < {}^1B_2$. This gives the following sequences:

$${}^1A_u < {}^1A_2 \ll {}^1B_2 < {}^1B_u$$

$${}^3B_2 < {}^3B_u \ll {}^3A_u < {}^3A_2$$

Thus, such simple considerations answer questions put forward in the literature.²¹

TABLE IV

Equilibrium Geometries and Relative Energies for the Ground and the Lowest Excited Singlet and Triplet States of Acetylene. The Linear Excited States are Presented in Order to Show Their Vertical Excitations

Electronic state	r_e (CC) (Å)	r_e (CH) (Å)	θ_e (CCH) (deg)	E (eV)
${}^1\Sigma_g^+$	1.200 (1.208) ^a	1.060 (1.058) ^a	180.0 (180.0) ^a	0.0 (0.0) ^a
${}^1\Sigma_u^-$	1.200	1.060	180.0	6.67
1A_2	1.332	1.070 ^b	137.5	5.22
1A_u	1.356 (1.388) ^a	1.070 ^b	128.0 (120) ^a	4.82 (5.23) ^a
${}^3\Sigma_u^+$	1.200	1.060	180.0	5.25 (5.2) ^c
3B_2	1.317	1.070 ^b	130.5	3.21 (2.6—4.7) ^d
3B_u	1.320	1.070 ^b	131.0	3.43

^a Reference 28; ^b The same CH distance is used for excited states; ^c Reference 29; ^d Reference 30

The relative energies as well as geometry parameters of ground and excited states are listed in Table 4. As far as comparisons with experimental assignments are possible, the calculated results are in reasonable agreement.

Earlier calculations of Rydberg states of acetylene have assumed initial geometries (vertical transitions), but have shown that carefully extended diffuse basis sets are needed.¹⁸ In the present investigation the two lowest singlet and triplet Rydberg states were studied and the equilibrium CC distances determined. All these states are found to correspond to linear geometries; the structural parameters and energetic orderings are given in Table 5. Since these Rydberg states are above the dissociation limit, the calculated geometries may correspond to local minima.

TABLE V

Equilibrium Data and Relative Energies for the Lowest Rydberg States of Acetylene

Electronic state	r_e (CC) (Å)	E (eV)	
$^1\Pi_u$	1.242 (1.26) ^a	8.79 (8.16) ^b	8.21 ^c
$^1\Pi_g$	1.261	8.98	8.73 ^c
$^3\Pi_u$	1.242	8.46	8.10 ^c
$^3\Pi_g$	1.293	8.60	8.61 ^c

^a Reference 31; ^b Reference 28; ^c Reference 18

In Figure 2 the energies of the lowest excited singlet and triplet states are shown with respect to their calculated bond angles for *cis* and *trans* conformations. Do these local minima correspond to static or to dynamic structures? The energy barriers shown by solid lines in Figure 2 are so high that a static structure must be assumed for both 1A_u and 3B_2 . This is so despite the fact that the energy barrier in Figure 2 corresponds to the linear structure whereas the lowest transition state corresponds to a half bent — half linear structure which reduces the barrier by approximately a factor of two. Thus, it is likely that the singlet excited state will only be observable in the *trans* conformation as *cis* to *trans* conversion will occur very rapidly. The situation with the triplet is not as clear.

Vinylidene and its Excited States

Vinylidene ($H_2C=C$), a higher energy isomer of acetylene, has often been considered before in its singlet (1A_1) ground state.²²⁻²⁶ While the vinylidene-acetylene energy difference is not very sensitive to the level of ab initio theory employed, the calculated 1,2-H shift barrier connecting these two singlet isomers depends greatly on the size of the basis set and the extent of electron correlation corrections.^{22,26} It is likely that singlet vinylidene is not a local minimum, and rearranges to acetylene without activation.^{22,27}

The triplet 3B_2 state of vinylidene, although estimated to be about 42 kcal/mol higher in energy than the 1A_1 singlet,²² is the form which is experimentally observable because the 1,2-H shift barrier is quite high.²⁷ Other

excited state configurations have been considered by Davis, Goddard, and Harding.²³ However, these authors only examined vertical transitions, and did not reevaluate the geometries of the higher excited states. Vertical excitation energies for vinylidene also were calculated by Dykstra and Schaefer.²⁴

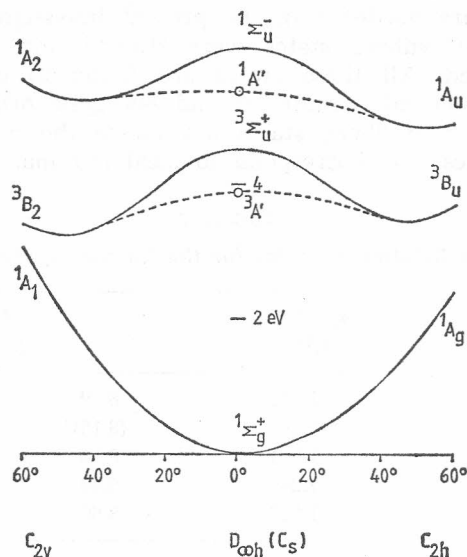


Figure 2. Energy for ground and lowest excited singlet and triplet states as a function of angle bending from linearity. Linear transition state ($D_{\infty h}$): full lines; bent transition state (C_s): dashed lines. The geometries of Table IV are used.

TABLE VI

Equilibrium Geometries and Energies of Vinylidene and Acetylene in Ground and Excited States

Vinylidene				Acetylene			
State	r_e (CC) (Å)	θ_e (HCH) ^a (deg)	E (kcal/mol)	State	r_e (CC) (Å)	θ_e (HCC) ^a (deg)	E (kcal/mol)
1A_1 (C_{2v})	1.298	118.8	35.9 ^b	$^1\Sigma_g^+$ ($D_{\infty h}$)	1.203	180	0.0 ^b
1A_1 (C_{2v})	1.291	118.6	39.3 ^c	$^1\Sigma_g^+$ ($D_{\infty h}$)	1.203	180	0.0 ^c
1A_2 (C_{2v})	1.402	114.0	110.8	1A_u (C_{2h})	1.353	127.4	110.4
1B_2 (C_{2v})	1.328	120.0	136.3	1B_2 (C_{2v})	1.335	134.2	120.4
3A_2 (C_{2v})	1.406	114.2	95.1	3A_u (C_{2h})	1.352	126.0	92.8
3B_2 (C_{2v})	1.304	116.0	73.3	3B_2 (C_{2v})	1.325	130.5	73.6

^a The CH bond lengths were fixed at 1.06 Å; ^b SCF approach, total energy -76.71702 a. u.; ^c with electron correlation corrections, total energy -77.18422 a. u.

Our calculations on vinylidene ground and excited states are compared with those for acetylene in Table 6. In agreement with earlier results,²² the energy of the 1A_1 ($H_2C=C$) state is 36–39 kcal/mol higher than that of the acetylene ground state ($^1\Sigma_g^+$) at both HF and correlated levels. However, the

energy differences between corresponding excited states are much smaller. Indeed, both the lowest triplet (3B_2) and the lowest singlet (1A_2) excited states of vinylidene are calculated to have nearly the same energy as the lowest triplet (3B_2) and lowest singlet (1A_u) excited states of acetylene, respectively. The 3A_2 state of vinylidene is only a little above the second triplet state (3A_u) of acetylene.

All vinylidene states have C_{2v} symmetry, and there is little variation in the HCH bond angles. Due to the partial occupancy of a π^* -type orbital (b_1), the 1A_2 and 3A_2 states have elongated C—C bonds (1.40 Å vs about 1.30 Å in all the other states). The C—C bond lengths in the excited states of acetylene are longer than in the ground state for similar reasons.

$C_2H_3^+$

Since the first explorations of protonation of acetylene and ethylene by quantum chemical procedures,³ many investigations have been concerned with the crucial question of reactive stabilities of classical and non-classical (bridged) structures.⁴⁻⁹ At high theoretical levels, the bridged form of the vinyl cation is more stable, but only by a few kcal/mol. If there is an energy barrier between these structures, it must be quite small, approximately 1 kcal/mol.⁷ Hence, protonated acetylene is a fluxional system in the ground state. The three protons move rapidly around the CC fragment, but all atoms remain in a plane (Figure 3). The equilibrium structures (Figure 4) with the basis set employed here which included additional d-type polarization functions at the carbon atoms, are presented in Table 7. In electronically excited states

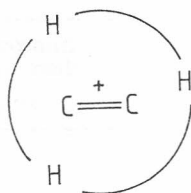


Figure 3. Schematic representation of the dynamic structure of $C_2H_3^+$ in the ground state; all atoms are in the same plane.

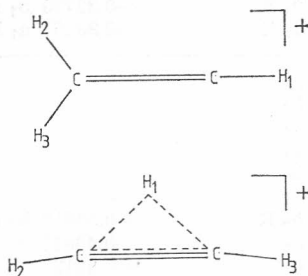


Figure 4. Classical and bridged structures of $C_2H_3^+$ in the ground state.

the »classical« and bridged structures are expected to exhibit much larger energy differences. As is well precedented, our SCF results with the augmented 4-31G basis set favor the classical structure (Figure 4). The calculation of both classical and bridged structures in the given geometries were also carried out with the larger 6-311G** triply split valence basis set (which includes p-type functions on hydrogen) with electron correlation corrections using our standard procedure. The two forms are practically isoenergetic, in general agreement with the literature.

TABLE VII

Equilibrium Geometries and Relative Energies for the Ground State of C₂H₃⁺ in Classical and Bridged Conformations (cf. Figure 4)

Structure	r_e (CC) (Å)	r_e (CH ₂) (Å)	r_e (CH ₁) (Å)	Θ_e (CCH ₂) (deg)	E (kcal/mol)
classical	1.272	1.082	1.070	120.0	0.0
bridged	1.211	1.070	1.296	177.8	10.6 ^a

^a This value was reduced by an improved basis set (6-311G**) and with electron correlation corrections to 2.5 kcal/mol.

TABLE VIII

Orbital Energies (a. u.) for the Classical and the Bridged Structures of C₂H₃⁺ (cf. Figure 4) Using the Geometries from Table 7

	Doubly occupied (valence) and vacant SCF orbitals	Improved virtual orbitals when b_1 is singly occupied		
		singlet	triplet	
classical	-1.37401 a_1			
	-1.09338 a_1			
	-0.95759 a_1			
	-0.90534 b_2			
	-0.72953 b_1			
		-0.23902 b_2	-0.62711 b_2	-0.66084 b_2
	-0.13275 $b_1 R$	-0.32750 $b_1 R$	-0.55372 b_1	
	-0.08561 $a_1 R$	-0.30257 $a_1 R$	-0.32920 $a_1 R$	
bridged	-1.43954 a_1			
	-1.07559 b_2			
	-0.99993 a_1			
	-0.87374 a_1			
	-0.75159 b_1			
		-0.13995 $b_2 R$	-0.50619 $b_2 R$	-0.54655 a_2
		-0.12017 a_2	-0.40041 a_1	-0.53131 $b_2 R$
	-0.10992 a_1	-0.32137 a_2	-0.41684 a_1	

R: Rydberg orbitals

In Table 8 doubly occupied, vacant, and singly occupied molecular orbitals are represented for the vinyl cations in their ground state geometries. The procedure used is the same as that of Table 1. For the classical structure the vacant orbitals as well as improved virtual singlet and triplet orbitals show a common ordering. For the bridged structure, all three sets of orbitals have different orderings. The vertical excitation energies for both structures are listed in Table 9. For the 1A_2 state the transition energies are in qualitative agreement with recently reported values.⁷

TABLE IX
Vertical Electronic Transition Energies of $C_2H_3^+$

Electronic state	E (eV)	
	classical	bridged
1A_2 ($b_1 \rightarrow b_2$)	2.79	6.68
1A_1 ($b_1 \rightarrow b_1$)	10.94	—
1B_1 ($b_1 \rightarrow a_1$)	11.62	9.56
1B_2 ($b_1 \rightarrow a_2$)	—	11.71
3A_2 ($b_1 \rightarrow b_2$)	1.87	5.99
3A_1 ($b_1 \rightarrow b_1$)	4.78	—
3B_1 ($b_1 \rightarrow a_1$)	10.89	9.11
3B_2 ($b_1 \rightarrow a_2$)	—	5.58

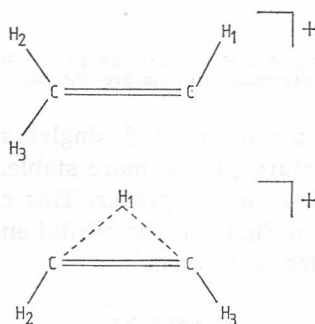


Figure 5. Classical and bridged structures of $C_2H_3^+$ in the lowest excited state.

TABLE X
Equilibrium Geometries and Relative Energies for the Classical and Bridged Structures of $C_2H_3^+$ in the Lowest Excited Singlet States (cf. Figure 5)

State	Structure	r_e (CC) (Å)	r_e (CH ₂) (Å)	r_e (CH ₁) (Å)	Θ_e (CCH ₁) (deg)	Θ_e (CCH ₂) (deg)	E (kcal/mol)
${}^1A''$	classical	1.380	1.079	1.068	147	121.3	0.0
1A_2	bridged	1.370	1.082	1.338	59	149.0	77.8

In searching for the equilibrium structures for excited states, symmetry reduction was taken into account. For the lowest singlet excited states of the classical (${}^1A''$) and the bridged (1A_1) species, the equilibrium structures

are shown in Figure 5 and in Table 10. The classical excited state (${}^1A'$) has a *bent* structure and is considerably stabilized with respect to the bridged excited state (1A_2), in which the acetylene moiety is bent markedly but the overall symmetry (C_{2v}) is retained. The Walsh diagram (Figure 6) explains why out-of-plane bending is not found. For the lowest triplet state (${}^3A''$), geometry parameters are essentially the same as are reported in Table 10 for the ${}^1A''$ singlet state. Only the change in the CCH_1 angle (to 139°) is significant. The ordering of electronic states (using the bent ${}^1A''$ geometry for all calculations) indicates the energy of the ${}^3A''$ triplet state to be only 0.07 eV higher than the singlet ${}^1A'$ bent ground state; the ${}^1A''$ energy is 1.48 eV higher.

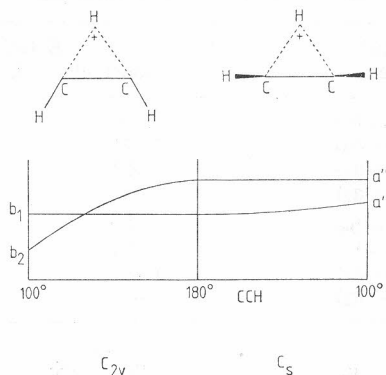


Figure 6. Walsh diagram for bridged $C_2H_3^+$ structures in the lowest excited state. The singly occupied orbitals are shown.

The situation for the second excited singlet states (Table 11) is quite different. The bridged structure (1B_1) is more stable. The »classical« structure of the second excited state ${}^1A'$ is not planar. This can be rationalized by the orbital correlation diagram in Figure 7; the orbital energies reflect the ordering of total energies of the states quite well.

TABLE XI

Equilibrium Geometries and Relative Energies for the Classical and Bridged Structures of $C_2H_3^+$ in the Second Excited Singlet State (cf. Figure 7)

State	Structure	r_e (CC) (Å)	r_e (CH ₂) (Å)	r_e (CH ₁) (Å)	θ_e (CCH ₁) (deg)	θ_e (CCH ₂) (deg)	E (kcal/mol)
${}^1A'$	classical	1.380	1.083	1.078	126	120	0.0
1B_1	bridged	1.250	1.065	2.095	73	180	-64.6

The calculated proton affinity of C_2H_2 based on the neutral and cation ground states is 164 kcal/mol, in agreement with other calculations.⁴ Proton affinities for excited states can be defined when the symmetry of the wave-

-functions of the neutral system and the cation can be correlated. However, with ionic-neutral comparisons, symmetry arguments are questionable. Nevertheless, comparison of total energies for excited states listed in Table 12 suggests a marked increase in the proton affinity with respect to that of the ground state.

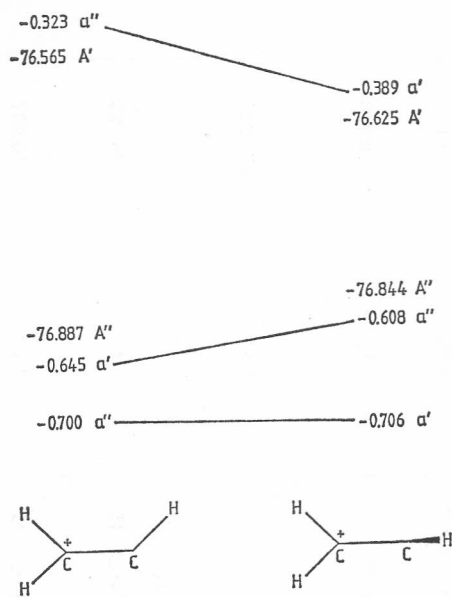

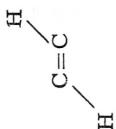
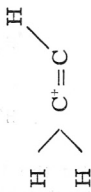
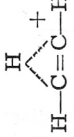
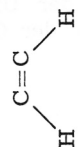
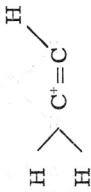
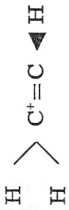


Figure 7. Orbital diagram and state diagram for the lowest excited states of classical C_2H_3^+ . Excitations come from the lowest orbital. (Energies in a. u.)

The triplet vinyl cation (${}^3A''$) should be an attractive target for experimental study. Its energy is indicated (Table 12) to lie only about 32 kcal/mol (1.39 eV) above that of the vinyl cation ground state, which is known experimentally to have $\Delta H_{fo}^0 = 266$ kcal/mol. Hence ΔH_{fo}^0 (C_2H_3^+ , ${}^3A''$) should be about 298 kcal/mol; this corresponds to a relatively low ionization potential of 10.3 eV from the vinyl radical (The IP of C_2H_4 is 10.51 eV). The triplet vinyl cation also has a similar structure to that of the vinyl radical (e. g.; $\angle \text{HCC} = 139^\circ$ and 135° , respectively), except that the latter has a somewhat shorter C—C bond (1.38 Å vs 1.33 Å) due to the presence of two instead of one π electron.

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TABLE XII
 Proton Affinities (E_{PA}) of C_2H_2 in Ground and Excited States

Structure	C_2H_2 State	E (a. u.)	Structure	$C_2H_3^+$ State	E (a. u.)	E_{PA} (kcal/mol)
$H-C\equiv C-H$	$1\Sigma_g^+$	-76.717		$1A_1$	-76.978	164
	$1A_u$	-76.540		$1A''$	-76.887	218
$H-C\equiv C-H$	$1\Pi_u$	-76.394		$1B_1$	-76.728	210
	$3B_2$	-76.599		$3A''$	-76.927	206
				$3A'$	-76.851	158

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SAŽETAK

Acetilen, viniliden i vinil kation u osnovnom i pobuđenim stanjima

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Prikazani su rezultati ab initio računa za klasične i premoštene geometrije acetilena, vinilidena i vinil kationa, $C_2H_3^+$. Izračunane su energije prijelaza elektrona, te ravnotežne geometrije temeljnih i niže pobuđenih elektronskih stanja. Za objašnjenje struktura pobuđenog stanja acetilena predložen je Walsh-ov dijagram. Dok je acetilen u temeljnom stanju stabilniji od vinilidena, energije nekoliko odgovarajućih pobuđenih stanja su im približne. Stabilnost premoštenih i klasičnih struktura vinil kationa vrlo je slična u temeljnom stanju, ali u različitim pobuđenim stanjima pojedina struktura može prevladavati. Afinitet prema protonu mora biti znatno manji u temeljnom nego u pobuđenim stanjima acetilena.