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Articles

The $C_4H_5^+$ Potential Energy Surface. Structure, Relative Energies, and Enthalpies of Formation of Isomers of $C_4H_5^+$

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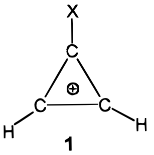
The potential energy surface for $C_4H_5^+$ as calculated by *ab initio* molecular orbital theory is reported at two levels of theory, HF/6-31G(d,p) and MP2(full)/6-311G(d,p). Fourteen minima have been located at HF/6-31G(d,p), but inclusion of electron correlation reduced this number to nine. The methylcyclopropenyl cation, **1**, is the global minimum, and the 2-cyclobutenyl (**2**), α-vinylvinyl (**3**), γ-methylpropargyl (**4**), α-methylpropargyl (**5**), and 1-cyclobutenyl (**6**) cations are 9.1, 19.9, 25.3, 27.5, and 26.9 kcal/mol, respectively, above **1**. Eleven transition structures, permitting interconversion between the nine minima, are reported. Enthalpies of formation (in kcal/mol) calculated at MP4SDTQ/6-311++G(2df,p) are 231.4 for **1**, 241.7 for **2**, 246.9 for **3**, 255.7 for **5**, 259.9 for **6**, and 264.3 for **7**.

Introduction

There is a wealth of experimental data, both from the gas phase and from solution, on the hydrocarbon cations $C_nH_m^+$. In solution, many of these ions are formed at low temperature in strong acid solutions, and the carbocations have frequently been characterized by NMR.[1−4] In the gas phase, the reactions of carbocations produced by electron impact on hydrocarbons have been studied extensively.[5] Small hydrocarbon cations are also found in flames,[6] and highly unsaturated ions have been detected in interstellar clouds.[7]

One of the most ubiquitous ions in gas phase hydrocarbon chemistry has the molecular formula $C_3H_3^+$. The cyclopropenyl ion, **1** with X = H, is the global minimum on this potential energy surface, and aromatic ion **1** has remarkable stability despite the large ring strain associated with the small unsaturated ring. By contrast, the isomeric open structure, the propargyl cation (**4** and **5** with X = H), despite the fact that the charge is delocalized over two carbon atoms, lies 25 kcal/mol higher in energy than **1**.[8a] Methyl substituents usually function as π-electron donors and stabilize carbocations, but substitution by a methyl group in the cyclopropenyl cation is likely to have little effect as π-donation disrupts the 2π-electron aromaticity of the ring. By contrast, a methyl substituent should stabilize the propargyl cation.[10] Consideration of these substituent effects stimulated our interests in isomers on the $C_4H_5^+$ potential energy surface. Preliminary investigation of the surface quickly revealed that other isomers not containing methyl groups, but rather having the charge stabilized by allyl and vinyl groups, are of similar energy to the methylcyclopropenyl and methylpropargyl cations. The $C_4H_5^+$ potential energy surface then has several minima, and the objective of this study is to determine the structures



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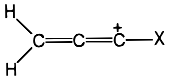

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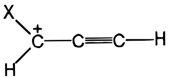

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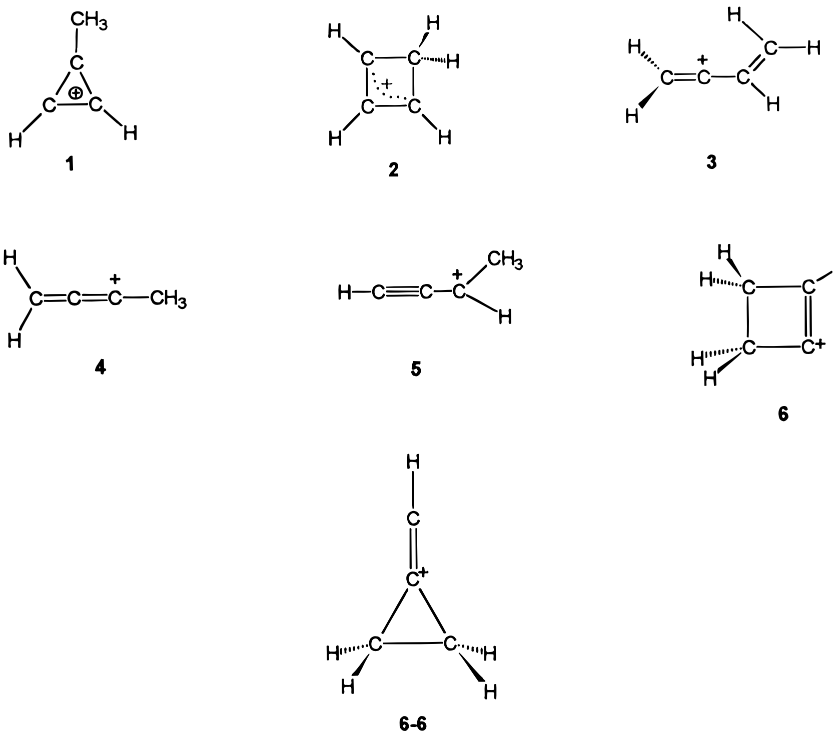

Figure 1. Low-lying isomers on the $C_4H_5^+$ surface.

and relative energies of these isomers and to find which, if any, of the higher energy isomers has a high barrier to rearrangement and may therefore be observable in the gas phase.

Several isomers of $C_4H_5^+$ have been characterized experimentally. Structural formulas for these ions are given in Figure 1. The methycyclopropenyl cation, **1**, has been postulated as the possible common ion derived from a series of small unsaturated hydrocarbons in the gas phase.[11] The 2-cyclobutenyl cation, **2**, is formed at low temperatures in solution and has been characterized by NMR.[1] This ion owes its stability to homoaromaticity[12] and has recently been the subject of an extensive theoretical study.[13] Deprotonation of **2** could, in principle, form tetrahedrane.[14]

Ion **3** is a vinyl cation substituted at the α-position by a vinyl group. This ion has not been observed in solution, but several methyl-substituted derivatives are transient intermediates in solvolysis[15] and have been characterized by NMR.[2] An experimental enthalpy of formation for the gas phase ion **3** has been deduced from appearance energies.[16]

Ions **4** and **5** are methyl-substituted propargyl cations, and trisubstituted propargyl ions are known in solution.[3] Enthalpies of formation of the alkenyl carbenium ions **4** and **5**, derived from ionization of the corresponding radicals, have also been reported for the gas phase ions.[16]

Ion **6** has been generated in the gas phase by loss of bromine atom from the cyclobutenyl bromide radical cation.[17] There is also some experimental evidence for the transient existence of one additional isomer, the cyclopropylidenemethyl cation, structure **6-6**.[17] This ion was also postulated as an intermediate in solvolysis reactions.[18]

There have been several theoretical studies of various isomers on the $C_4H_5^+$ potential energy surface. Initially, *ab initio* molecular orbital calculations at HF/STO-3G were reported for ions **4**, **5**, **6**, **6-6**, and **5-5**.[19] Subsequently, in a study of substituent effects in propargyl and cyclopropenyl cations, **1**, **4**, and **5** were examined at the HF/6-31G(d) level.[20] More recently, Schleyer[13] and Notario[14] have used correlated wavefunctions to study the inversion barrier, stability, and proton-donating power of the 2-cyclobutenyl cation, **2**. In summary, then, several of the isomers of $C_4H_5^+$ have been examined but at different levels of theory. In this study, in order to be consistent, we have examined all isomers and the transition structures to their interconversion at two levels of theory, HF/6-31G(d,p)[21] and then, in order to assess the effect of electron-correlation, at MP2(full)/6-311G(d,p).[22-24]

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Table 1. Total Energies (Hartrees) and Relative,[b] Zero-Point, and Thermal Energies (all in kcal/mol) from Structure Optimization Calculations

structure	HF/6-31G(d,p)	ZPE[a]	thermal	MP2/6-311G(d,p)	MP4/6-311++G(2df,p)
1	−154.077 36	43.7	2.9	−154.695 81	−154.758 01
2	−154.051 82 (16.6)	45.0	2.2	−154.682 21 (9.1)	−154.742 87 (10.1)
3	−154.045 35 (19.3)	43.0	2.8	−154.662 75 (19.9)	−154.732 33 (15.3)
4	−154.028 97 (29.3)	42.1	3.4	−154.653 74 (25.3)	
5	−154.024 01 (32.0)	42.5	3.2	−154.650 57 (27.5)	−154.718 04 (24.2)
6	−154.007 18 (44.1)	44.1	2.6	−154.653 17 (26.9)	−154.712 98 (28.4)
7	−154.003 63 (44.5)	42.4	2.4	−154.639 94 (33.3)	−154.702 93 (32.8)
8	−153.996 94 (48.9)	42.0	3.0		
9	−153.995 69 (50.3)	43.0	2.7		
10	−153.968 27 (67.1)	42.0	3.2		
11	−153.964 17 (69.5)	42.0	3.1	−154.563 06 (81.8)	
12	−153.955 47 (75.3)	42.2	3.2		
13	−153.937 52 (86.4)	42.9	2.4	−154.568 74 (78.4)	
14	−153.905 27 (104.3)	39.5	3.4		
$C_2H_2 + C_2H_3^+$	−153.906 27 (101.4)	36.8	3.8	−154.546 78 (87.5)	
$H(^1S)$					−1.167 76
$H_2(^1\Sigma_g^+)$					−0.499 82
$C(^3P)$					−37.776 39

[a] Zero-point vibrational energies (ZPE) are scaled by 0.89. [b] Relative energies in (kcal/mol) from the global minima are given in parentheses. These include zero-point energies and thermal corrections.

Table 2. Total Energies (Hartrees) and Relative,[b] Zero-Point, and Thermal Energies (all in kcal/mol) for Transition Structures

transition structures	HF/6-31G(d,p)	ZPE[a]	thermal	MP2/6-311G(d,p)	ZPE[a]
[**1**−**7**]	−153.957 78 (72.2)	41.4	2.4	−154.592 25 (62.2)	43.6
[**2**−**7**]	−154.002 78 (45.5)	43.0	2.3	−154.639 37 (34.1)	45.1
[**2**−**11**]	−153.916 61 (97.5)	40.0	2.3	−154.554 27 (84.5)	43.7
[**3**−**4**]	−153.973 14 (62.2)	40.6	2.8	−154.603 04 (55.0)	43.0
[**3**−**6**]	−153.985 99 (56.0)	42.9	2.4	−154.626 51 (42.2)	45.3
[**3**−**7**]				−154.604 39 (54.5)	44.0
[**3**−**8**]	−153.994 32 (49.2)	40.9	2.8		
[**3**−**9**]	−153.993 27 (51.3)	42.6	2.5		
[**5**−**5**]	−153.982 83 (57.1)	41.7	2.7	−154.607 09 (53.5)	43.5
[**5**−**6**]	−153.979 57 (59.6)	42.2	2.7	−154.601 51 (57.4)	44.2
[**6**−**6**]	−154.004 71 (44.4)	43.0	2.4	−154.641 61 (32.8)	46.1
[**6**−**11**]	−153.884 54 (118.1)	41.3	2.4	−154.541 72 (93.8)	43.8
[**6**−**13**]	−153.891 66 (111.3)	39.0	2.4	−154.535 29 (95.5)	43.8
[**7**−**8**]	−153.988 65 (53.5)	41.7	2.7		

[a] Hartree−Fock zero-point energies are scaled by 0.89, and MP2 values are unscaled. [b] Relative energies (kcal/mol) from the global minima are given in parentheses. These include zero-point energies and thermal corrections taken from HF level calculations.

Computational Methods. *Ab initio* molecular orbitals calculations were performed using Gaussian 86,[25a] Gaussian 90,[25b] and Gaussian 92.[25c] Full structure optimizations using gradient techniques[26] were carried out at the HF/6-31G(d,p) and MP2 (full)/6-311G(d,p) levels. Single-point calculations at MP4(fc)SDTQ using the 6-311++G(2df,p) basis set were performed on structures optimized at the MP2(full)/6-311G(d,p) level. All critical points on the Hartree−Fock surface were characterized by harmonic vibrational frequency calculations. Transition structures were located with the aid of the CalcAll routine, and the intrinsic reactions coordinate (IRC) routine[26] was used to establish which two minima are associated with each transition structure. Total energies for the minima are given in Table 1 and for the transition structures in Table 2. The ions have been numbered in order of increasing energy as determined at the Hartree−Fock level. Each transition structure is denoted in terms of the two minima with which it is associated.

Results and Discussion

(a) Structural Details. Full structural optimizations were performed without the use of symmetry. Structural parameters, for simplicity involving only the carbon atoms, are shown in Figures 2 (minima) and 3 (transition structures). In transition structures involving migration of a hydrogen atom or a rearrangement additional structural parameters associated with the migrating groups are shown.

The methylcyclopropenyl cation, **1**, is at the global minimum on the $C_4H_5^+$ surface. The methyl group functions as a weak electron donor, and this leads to a slight elongation (by 0.010 Å) of the vicinal bonds relative to those in the parent cyclopropenyl cation. Conversely, the distal bond is slightly shorter (by 0.005 Å). This effect

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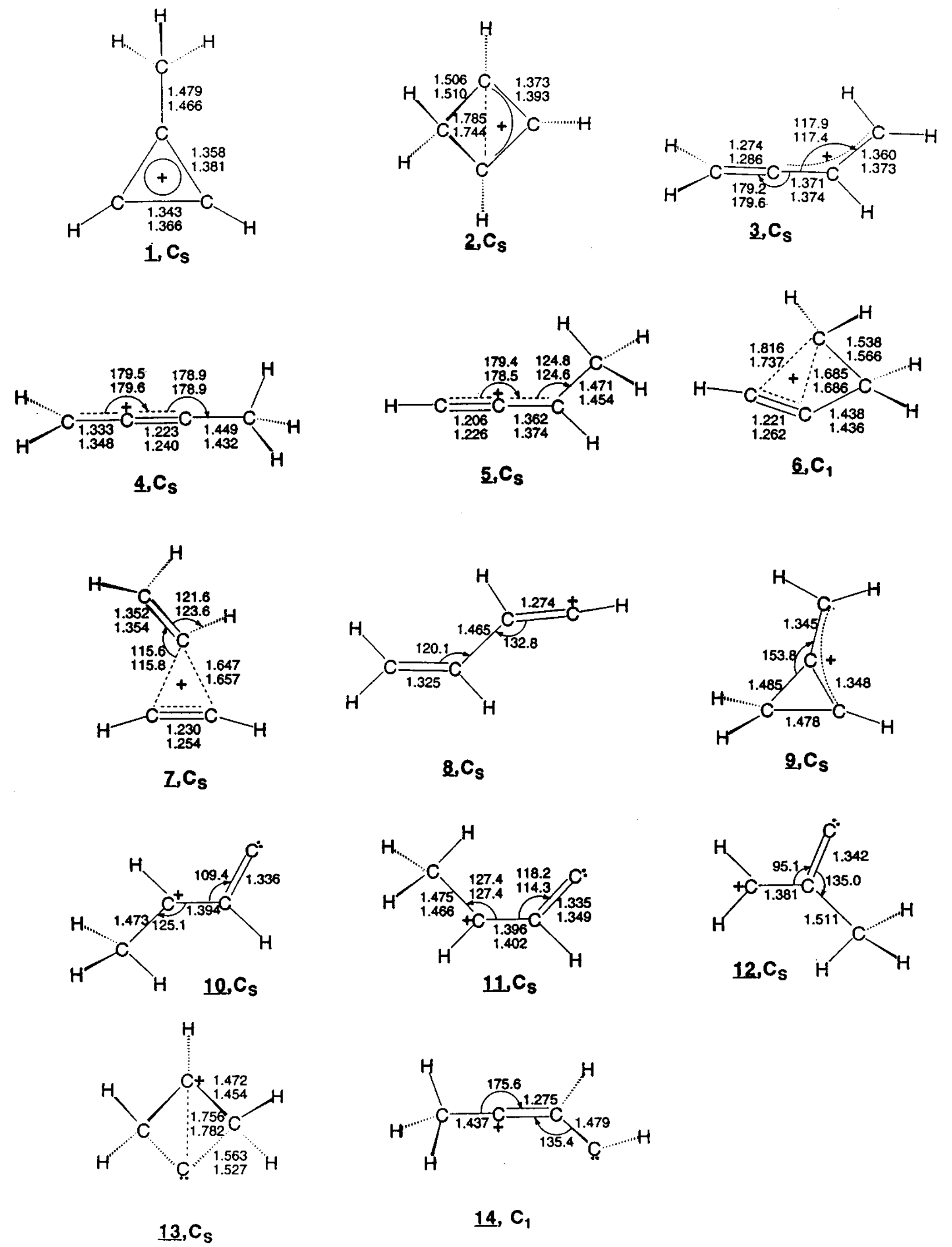
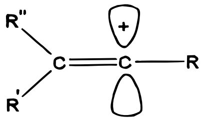


Figure 2. Optimized geometric parameters for $C_4H_5^+$ isomers. Upper numbers are from HF/6-31G(d,p) and lower numbers from MP2(full)/6-311G(d,p). Bond lengths are in angstroms and angles in degrees.

of electron donors on the structure of the cyclopropenyl cation has been noted previously.[20]

The 2-cyclobutenyl cation, **2**, owes its stability to homoaromaticity.[13] The cross-ring distance of 1.744 Å is considerably longer than a single C−C bond, whereas the bonds between the CH groups (1.393 Å) are similar to those in the allyl cation (1.384 Å).

Ion **3** is a vinyl cation with a vinyl substituent attached to the α-carbon. The vinyl cation formally has a vacant p-orbital on the cationic carbon in the plane of the methylene group (structure **3a**). Substituents that function as π-electron donors, when located on the α-carbon, adopt a conformation in which donation to the cationic carbon is maximized, and consequently, such substituents are strongly stabilizing.[19] For ion **3**, maximizing π-donation requires that the planes of the two methylene groups are at 90° to each other. In terms of resonance structures **3b** and **3c** the charge is delocalized on to two carbon atoms.



3a

From the resonance structures, it is apparent that **3** may also be described as being an allyl cation with one terminal carbon atom attached to a methylene group. The C−C distances in the allyl group in **3** are almost identical (Figure 2) and are ~0.010 Å shorter than in the parent allyl cation. The third C−C bond distance, 1.286 Å, is

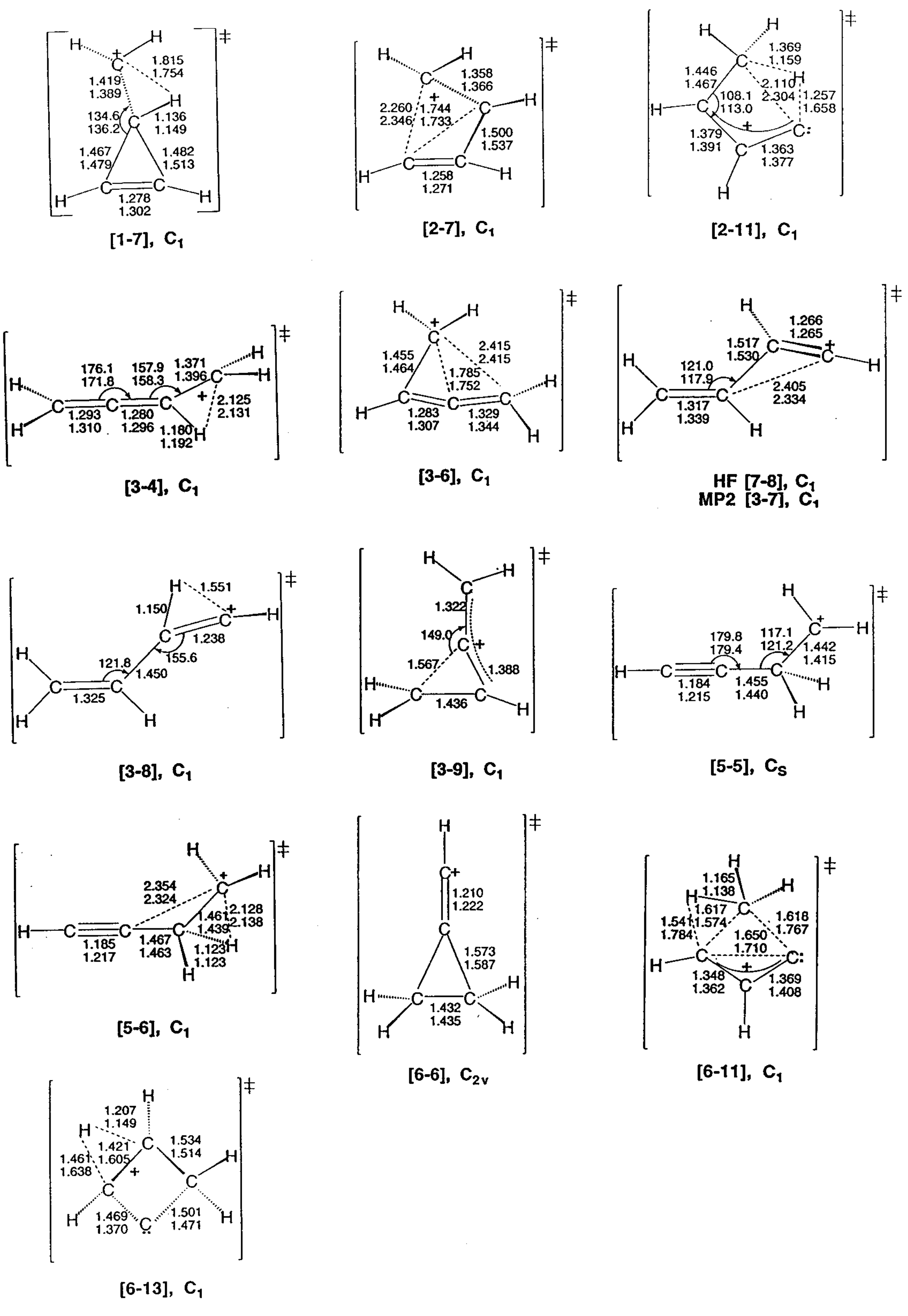
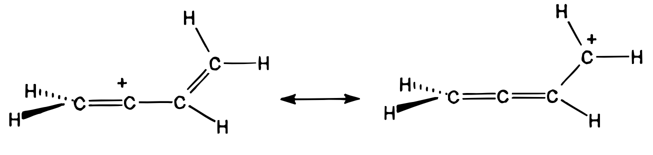


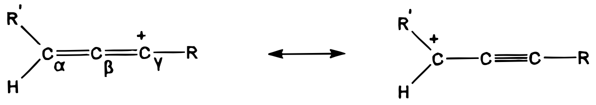
Figure 3. Optimized geometric parameters for transition structures on the $C_4H_5^+$ surface. Upper numbers are from HF/6-31G-(d,p) and lower numbers from MP2(full)/6-311G(d,p). Bond lengths are in angstroms and angles in degrees.



3b **3c**

slightly longer (by 0.025 Å) than that in the parent open vinyl cation.

Structures **4** and **5**, the methylpropargyl cations, have been the subject of a previous theoretical study.[20]



4a **4b**

A methyl group substituted on the γ-carbon (structure

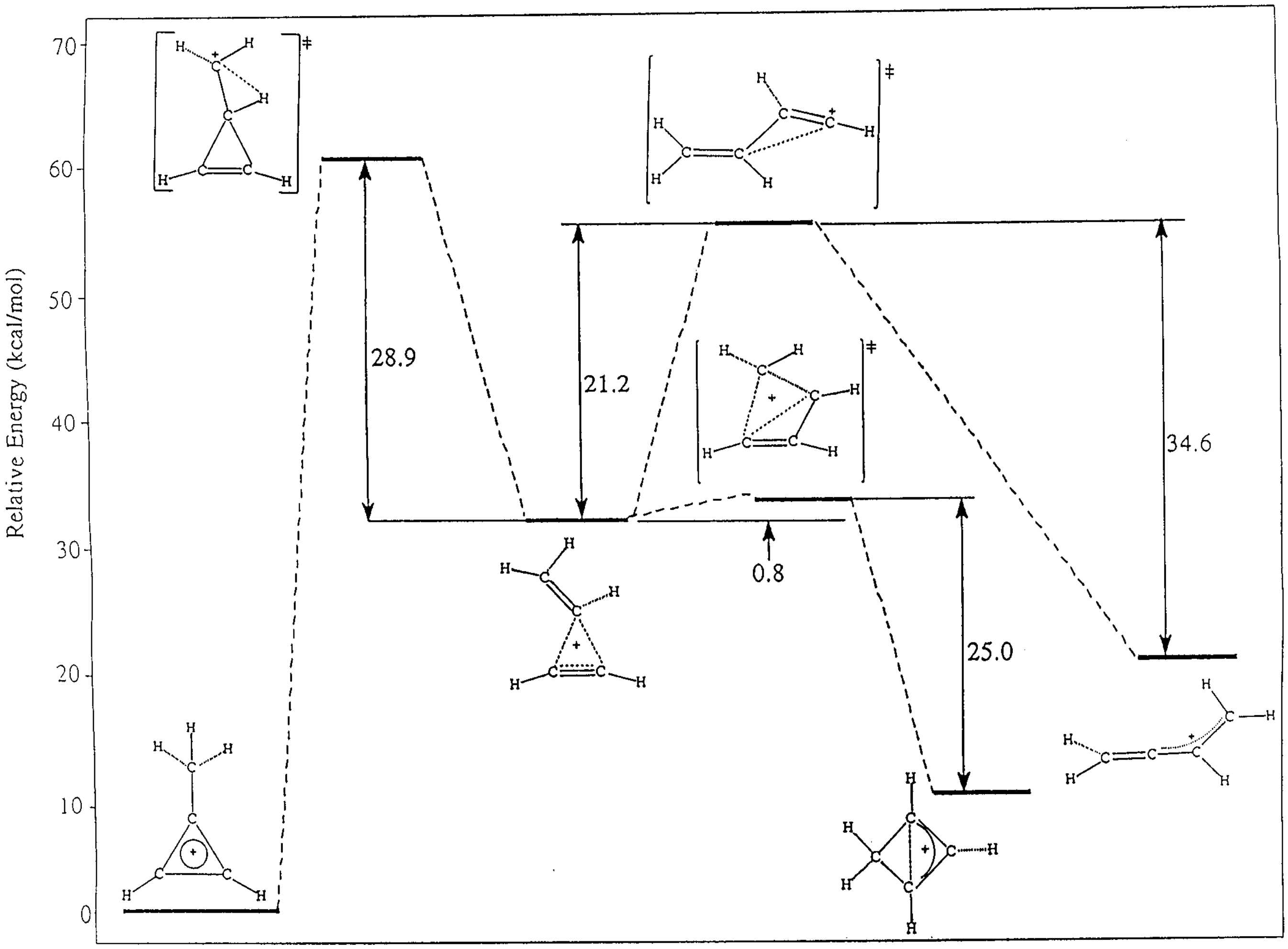
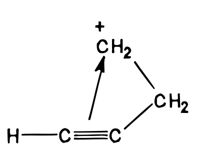


Figure 4. Reaction profile for interconversion of structures **1**, **7**, **2**, and **3** as calculated at the MP2/6-311G(d,p) level.

4, R = CH_3, R′ = H) has the effect of slightly elongating the $C_\beta-C_\gamma$ bond and shortening the $C_\alpha-C_\beta$ bond; i.e., structure **4a** is favored. The converse is true when the methyl group is attached to the α-carbon and structural **4b** is favored as in ion **5**.

The 1-cyclobutenyl cation, **6**, has extremely long distances for single bonds in the 3-membered ring containing the two dotted lines. This structure is best represented as a primary carbocation stabilised by π-donation from a terminal alkyne. As is common for nonclassical bridged ions, inclusion of electron correlation results in pronounced changes in the geometry of the ring. It also reduces the energy of this ion relative to those of the other isomers.



6

Ion **7** has the unusual structural feature of two long C−C bonds (1.657 Å). This ion is best described as a classical vinyl cation heavily stabilized by a solvating acetylene molecule. The dissociation energy of the ion−molecule complex is 56.9 kcal/mol at HF/6-31G(d,p) and 54.2 kcal/mol at MP2(full)/6-311G(d,p).

Ion **8**, a β-vinyl-substituted vinyl cation, has much higher energy than the α-vinyl-substituted isomer, **3**, because the vinyl group when substituted at the β-position cannot assist in delocalizing the charge. Structure **9** contains an allyl cation group constrained to being in a 3-membered ring. Ions **8** and **9** are of little importance since they both collapse via low barriers into ion **3**.

Ions **10**−**14**, all carbenes, are high energy species. Structures **10**, **12**, and **14** do not exist at the MP2/6-311G-(d,p) level, and the barrier to rearrangement for **11** → **2** is only 2.7 kcal/mol. Of these carbenes, only **13**, with a barrier of 17.1 kcal/mol to rearrangement to **6**, exists in a moderately deep potential well.

(b) Potential Energy Surface. At the HF/6-31G(d,p) level we located 14 minima and 14 transition structures for interconversion between the minima. Inclusion of electron correlation reduced the number of minima to nine, and for interconversion between these minima, we have found 11 transition structures. The surfaces as calculated at the MP2(full)/6-311G(d,p) level are shown in Figures 4−6.

The likelihood of any isomer being long-lived in the gas phase depends on the barriers to its interconversion with lower energy isomers. For this reason, we were particularly interested in finding transition structures for the interconversion of various isomers with the methylcyclopropenyl cation, the global minimum. We found only one

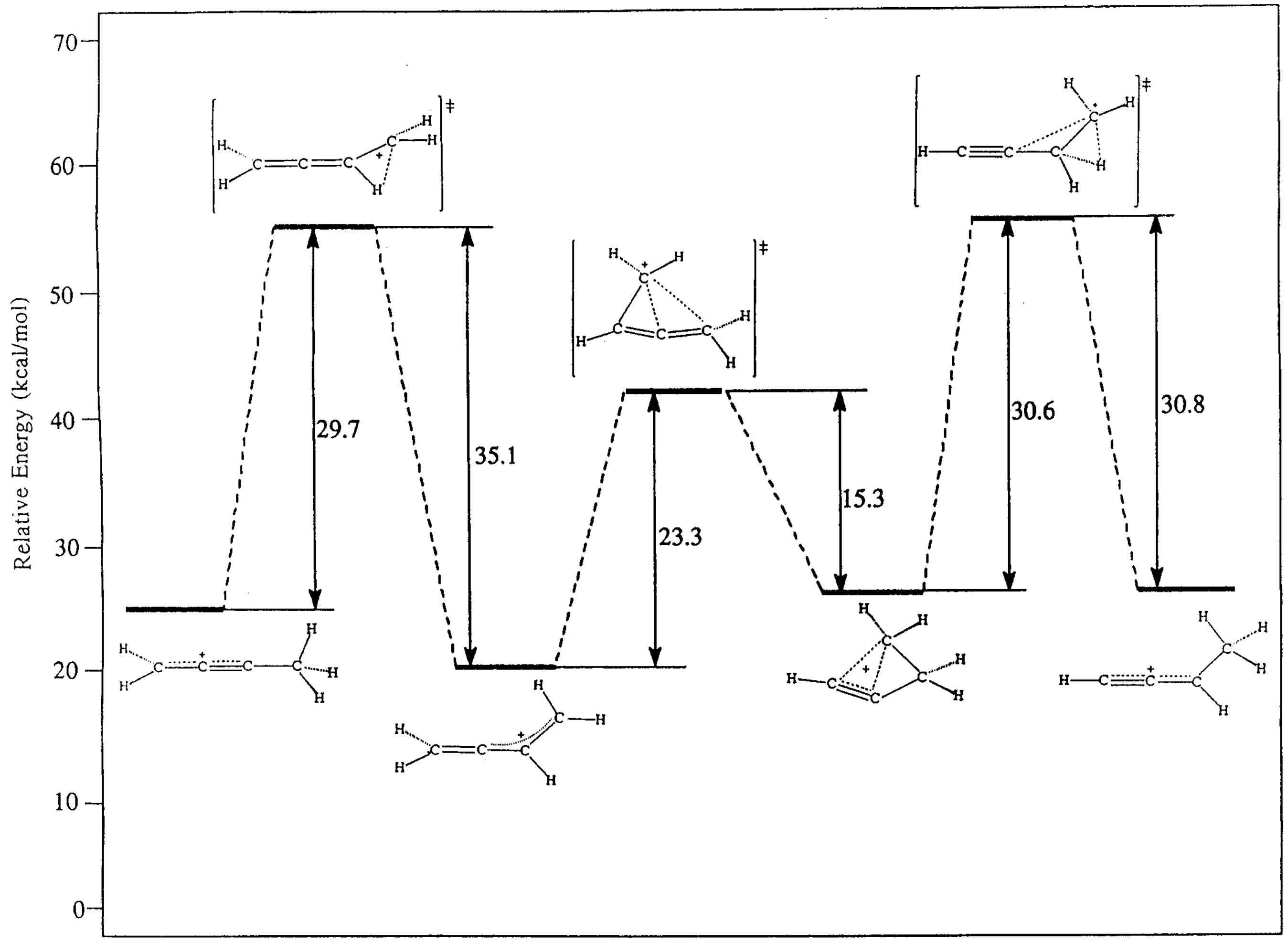
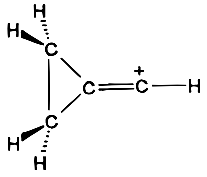


Figure 5. Reaction profile for interconversion of structures **4**, **3**, **6**, and **5** as calculated at the MP2/6-311G(d,p) level.

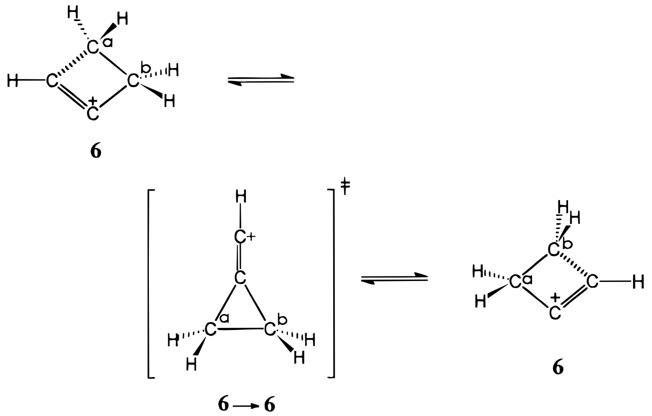
such transition structure, and this led to formation of isomer **7**, the vinyl cation solvated by acetylene. Transition structure **7** → **1** is 28.9 kcal/mol above **7** and 62.2 kcal/mol above **1** at the MP2(full)/6-311G(d,p) level.

Ion **7** can be formed from isomers **2** and **3**, and the transition structures for these reactions both lie below that for conversion of **7** and **1**. Structure **7**→**1** then is also the transition structure for conversion of **2** into **1** (with a barrier of 53.1 kcal/mol above **2**) and for formation of **1** from **3** (barrier 42.3 kcal/mol above **3**), as shown in Figure 4. Conversion of **3** into **2** requires the intermediacy of **7**, and the barrier to this process is 34.6 kcal/mol above **3**. From the magnitude of these barriers, we conclude that ions **1**−**3**, if formed in low-energy processes in the gas phase, will all be long-lived ions at room temperature.

Ions **4** and **5**, the methyl-substituted propargyl cations, both have substantial barriers to rearrangement (29.9 and 30.8 kcal/mol, respectively) and both form ion **3** (Figure 5). In the case of the α-methylpropargyl cation, the rearrangement involves ion **6** as an intermediate, but the latter has a lower barrier to formation of **3**. Despite the relatively low barrier (15.3 kcal/mol) for rearrangement of **6** into **3**, ion **6** has been formed in the gas phase by loss of Br from the radical cation resulting from ionization of 1-bromocyclobutene.[17] In a similar reaction, the cyclopropylidenemethyl cation, **15**, was reported to be formed, but to be sensitive to rearrangement to **6**.[17] In our calculations we were unable to locate a structure **15** that is at a minimum. Indeed, structure **15** proved to be a transition structure, **6** → **6**, 6.4 kcal/mol above **6**, for the scrambling of the two methylene groups in structure **6**.



15



6

6→6

6

The two carbenes, ions **11** and **13**, have low barriers to rearrangement (Figure 6). Ion **11**, in a rearrangement that involves a 1−4 H-shift and a cyclization, collapses

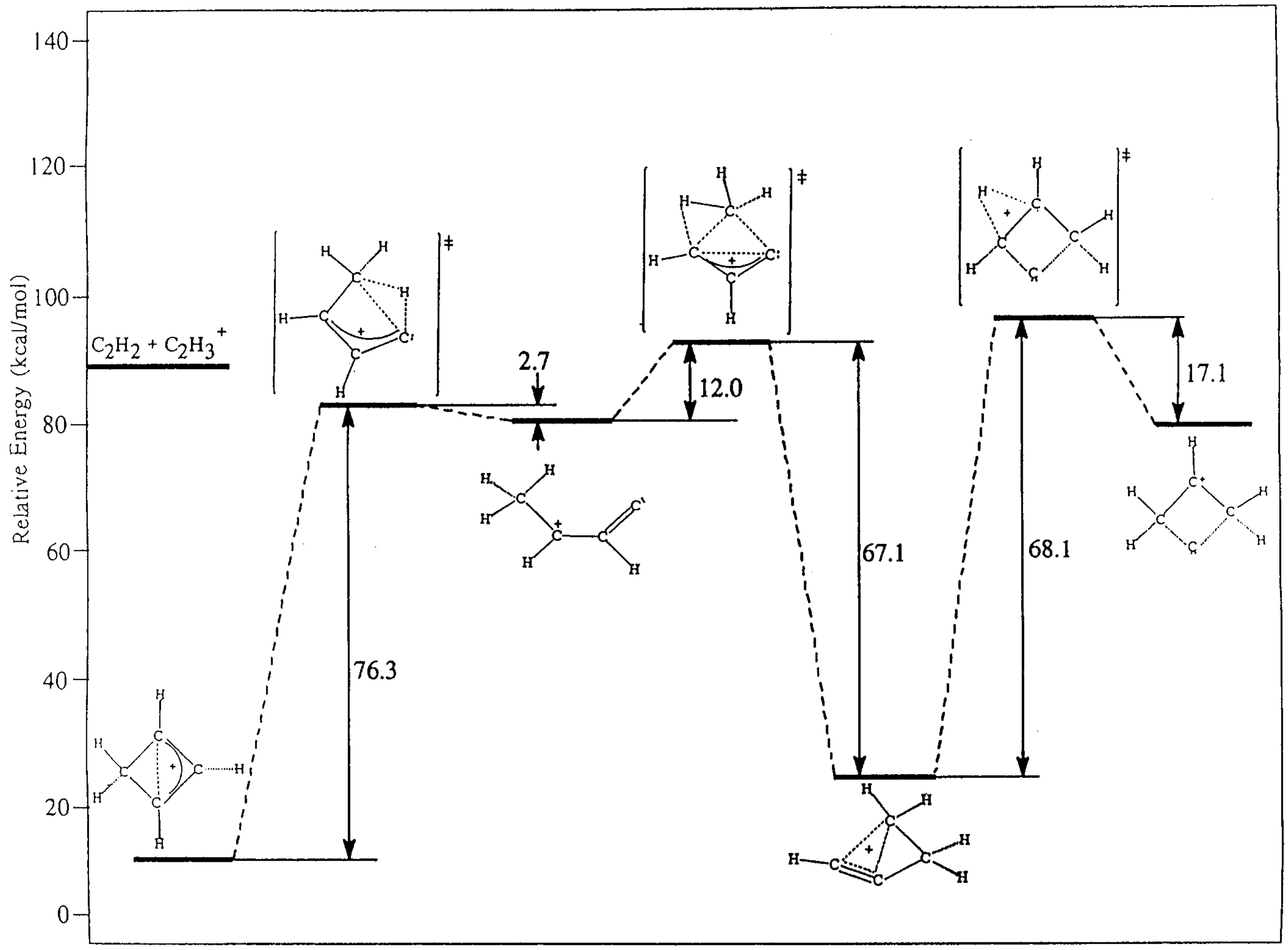


Figure 6. Reaction profile for interconversion of structures **2**, **11**, **6**, and **13** as calculated at the MP2/6-311G(d,p) level.

to **2** with a barrier of only 2.7 kcal/mol. Ion **13** rearranges to **6** with a barrier of 17.1 kcal/mol, but as transition structure **13** → **6** is higher than the barrier for **6** to rearrange to **1**, so **13** → **6** is effectively the transition structure for rearrangement of **13** to **1**.

(c) Enthalpies of Formation. *Ab initio* molecular orbital calculations at the G2 level[28] or using extended basis sets at MP4SDTQ or QCISD(T) levels of theory have been shown to consistently produce $\Delta H_{f,298}$ values within ±2 kcal/mol of the experimental values.[29] Enthalpies of formation of six isomers of $C_4H_5^+$ (Table 3) have been calculated by combining heats of atomization from MP4(fc)/6-311++G (2df,p) calculations with experimental enthalpies of formation of C and H, using a previously reported procedure.[30] For ions **3** and **5** the calculated enthalpies are within 1.3 kcal/mol^{-1} of the experimental values. However, for the methylcyclopropenyl ion the calculated enthalpy is 5.6 kcal/mol lower than the experimental value. The reasons for this discrepancy are not obvious. The experimental enthalpy of formation of the methylcyclopropenyl cation was obtained from the appearance energy of $C_4H_5^+$ by hydrogen atom and electron loss from a structurally dissimilar molecule, 1-butyne. On the basis of enthalpies of formation, the ion formed in this reaction is not **5**, but since **5** rearranges to **1** via the sequence **5** → **6** → **3** → **7** → **1** and the last step, **7** → **1**, has a much higher barrier (28.9 kcal/mol above **7**) than for the rearrangment **7** → **2** (0.8 kcal/mol above **7**), it is possible that the ion formed from 1-butyne is **2** and not **1** as previously claimed. If this is the case, then the calculated $\Delta H_{f,298}$ for **2** is only marginally closer to the experimental value reported for **1**, and the difference (4.7 kcal/mol) between theory and experiment is still much larger than normally experienced at this level of theory. In an attempt to resolve this situation we used the same procedure to calculate enthalpies of formation for **1** and **2** at an even higher level

Table 3. Enthalpies of Formation in (kcal/mol) at 298 K

structures	calcd	exptl[a]
1	231.4 (231.3)[b]	237
2	241.7 (241.7)[b]	
3	246.9	246
5	255.7	257
6	259.9	
7	264.3	

[a] Lossing, F. P.; Holmes, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 6917. [b] From QCISD(T)(full)/6-311G(d,p)//MP2(full)/6-311G(d,p). Total energies for **1** and **2** are −154.841 86 Hartrees and −154.826 36 Hartrees, respectively.

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of theory, QCI(full)SD(T)/6-311G(2df,p)//MP2(full)/6-311G-(d,p). This approach, however, did not provide any further insights as the QCI calculations gave enthalpies almost identical to those calculated at MP4.

Conclusions

Ab initio molecular orbital calculations show that six isomers of $C_4H_5^+$ have sufficiently low energies and high barriers to rearrangement that they are good candidates for observation in the gas phase. Experimental enthalpies of formation have been reported for four of these isomers, ions **1**, **3**, **4**, and **5**, and a fifth ion, the 1-cyclobutenyl cation, **6**, has been observed. The sixth isomer, the 2-cyclobutenyl cation, has the second best energy on the surface, and while not known in the gas phase, it has been characterized in strong acid solutions.

Ion **1** is stabilized by aromaticity, while ions **2**−**5** have elements of the allyl, vinyl, and allenyl cation structures contributing to their stabilities. Ion **6** is unusual in that it has very long bonds between one of the CH_2 groups and the two unsaturated carbons, while the multiple bond is very short. Ion **6** then is not well represented by a classical 4-membered ring structure. The two CH_2 groups in **6** equilibrate via the cyclopropylidenemethyl cation, which contrary to gas phase results, is a transition structure.

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