

# Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XXII. Structures and Stabilities of $C_3H_3^+$ and $C_3H^+$ Cations

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**Abstract:** Ab initio molecular orbital theory is used to study the relative energies of various isomers of  $C_3H_3^+$  and  $C_3H^+$ . Energy minimized geometries were obtained using the STO-3G minimal basis set; single calculations were then carried out using the larger 4-31G and 6-31G\* bases. The theory indicates that the cyclopropenium ion (I) is the most stable  $C_3H_3^+$  isomer with a resonance energy of more than 60 kcal/mol. The propargyl cation (II) is the next most stable form with an energy 34 kcal/mol above I. All other isomers were found to have considerably higher energies. The linear structure IX was found to be the most stable form of  $C_3H^+$ , but there is a considerable discrepancy between the calculated heat of formation (406 kcal/mol) and the available experimental data for this ion (280–360 kcal/mol).

## Introduction

The carbocation systems  $C_3H_3^+$  and  $C_3H^+$  are known experimentally and there has been some research on the structures and energies of the possible isomeric forms.<sup>2,3</sup>  $C_3H_3^+$  has received the most attention.<sup>2,3</sup> The cyclopropenyl (I) and propargyl (II) cations (Figures 1 and 2) have been studied in a number of ways.<sup>2,3</sup>

The cyclopropenyl cation (I) represents the simplest aromatic system with two delocalized  $\pi$  electrons and was consequently expected to exist as a relatively stable species. Derivatives of I were first detected by Breslow in 1957<sup>3a</sup> and crystalline salts of the parent ion have subsequently been synthesized.<sup>3b</sup> The  $pK_R$  value has also been measured.<sup>3b</sup> Some crystal structures containing cyclopropenyl cation derivatives have been determined and show an approximately equilateral triangle for the ring with bond lengths shorter than in benzene.<sup>3e,f,h</sup> Ab initio molecular orbital calculations have been reported by Clark<sup>4a</sup> and by Ha, Graf, and Günthard,<sup>4b</sup> but they did not include full geometry variation.

The propargyl cation II is also resonance stabilized and its existence has been postulated.<sup>3c,d</sup> In the gas phase, there was some early uncertainty in the identification of  $C_3H_3^+$  species but Lossing has recently presented evidence that propargyl cation (II) is significantly less stable than cyclopropenyl cation (I).<sup>3d</sup> There do not appear to have been any ab initio studies of the propargyl cation.

The  $C_3H^+$  species are less familiar and there is little evidence or even speculation about the structures involved. The ion has been detected in mass spectroscopy, but there is a wide range of proposed heats of formation which could correspond to various isomers or simply to experimental uncertainty.<sup>2</sup> No quantum mechanical studies have been reported.

In this paper, we describe an extensive ab initio molecular orbital study of both  $C_3H_3^+$  and  $C_3H^+$ , considering in detail a number of possible structures. The procedure used is to obtain structures by local minimization of the energy with a simple minimal basis set and then carry out single calculations with extended sets at these geometries. This set of energies can then be used to discuss the relative stabilities of the proposed isomeric structures. This follows closely previous work on other molecules and cations including various isomeric forms of  $C_3H_7^+$ <sup>5</sup> and  $C_3H_5^+$ .<sup>6</sup>

## Method

Standard ab initio LCAO-SCF molecular orbital theory is used.<sup>7</sup> For each structure of interest, we obtain an optimized geometry by specifying a symmetry and, where necessary, other constraints that define the particular structure, and then minimizing the total energy with respect to all remaining geometric parameters. This procedure is carried out using the minimal STO-3G basis set<sup>8</sup> which has proved quite successful in reproducing and predicting geometries for a large number of neutral molecules.<sup>9</sup> Single calculations at these optimized geometries are then carried out with the split-valence 4-31G basis set<sup>10</sup> which is more successful for energy comparisons. However, even the 4-31G basis is not entirely satisfactory for the determination of relative energies of small-ring cyclic vs. acyclic molecules and it has been found that addition of polarization functions, particularly d functions on carbon, to the basis set leads to much better results.<sup>5,11</sup> We have, therefore, also carried out such calculations (using the 6-31G\* basis set<sup>11</sup>) in a limited number of cases. There are indications that correlation corrections may be important, but these were not considered in this study.

## Results and Discussion

**$C_3H_3^+$  Cations.** Calculated energies for the  $C_3H_3^+$  cations are listed in Table I. These are now discussed together with the theoretical structures.

**Cyclopropenium Ion (I).** Our calculations show that I with  $D_{3h}$  symmetry is the lowest energy form of  $C_3H_3^+$ . The theoretical carbon-carbon bond length is 1.377 Å (Table II) in close agreement with experimental<sup>3e,f</sup> bond lengths (1.363 and 1.373 Å) for derivatives of I. Both the theory and experiment indicate that the C=C bonds in the cyclopropenyl cation are slightly shorter than in benzene (calculated<sup>12</sup> and experimental<sup>13</sup> values of 1.39 and 1.397 Å, respectively).

The theoretical energies may be used to make an estimate of the heat of formation of the cyclopropenyl cation. For reaction 1, the theoretical energy change is 91.1 kcal



mol<sup>-1</sup> (6-31G\*), using previously reported results.<sup>11</sup> If we combine this with the known experimental heats of forma-

Table 1. Calculated Energies for  $C_3H_3^+$  Cations

Cation	STO-3G		4-31G		6-31G*	
	Total, hartrees,	Relative, kcal mol <sup>-1</sup>	Total, hartrees	Relative, kcal mol <sup>-1</sup>	Total, hartrees	Relative, kcal mol <sup>-1</sup>
I Cyclopropenyl	-113.62032	0	-114.81364	0	-115.00369	0
II Propargyl	-113.56391	35.4	-114.78923	15.3	-114.94894	34.4
III Prop-2-en-1-yl-3-ylidene	-113.51319	67.2	-114.72582	55.1	-114.89283	69.6
IV Perpendicular prop-2-en-1-yl-3-ylidene	-113.45112	106.2	-114.67176	89.0	-114.83927	103.2
V 1-Propynyl	-113.43715 <sup>a</sup>	114.9	-114.63828 <sup>a</sup>	110.0		
VI Cycloprop-1-yl-2-ylidene	-113.42399	123.2	-114.60974	128.0		
VII Prop-1-yl-1,3-diylidene	-113.37232	155.6	-114.56726	154.6		
VIII Corner protonated cyclopropyne	-113.34084 <sup>a</sup>	175.4	-114.52079 <sup>a</sup>	183.8		

<sup>a</sup>The best wave function is complex.

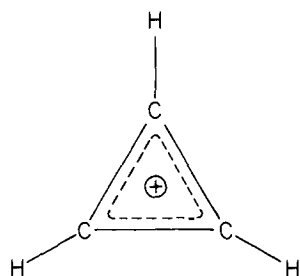
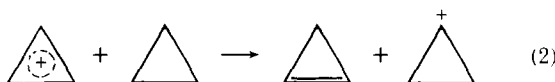


Figure 1. Cyclopropenyl cation (I).

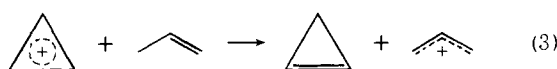
tion<sup>14</sup> for methane ( $-17.9$  kcal mol<sup>-1</sup>), cyclopropene ( $+66.6$  kcal mol<sup>-1</sup>), and methyl cation ( $+260$  kcal mol<sup>-1</sup>), we obtain a value of  $253$  kcal mol<sup>-1</sup> for  $\Delta H_f^\circ$  (cyclopropenyl cation). This is in good agreement with the recent experimental value of  $256 \pm 2$  kcal mol<sup>-1</sup>.<sup>3d</sup>

It is of interest to find whether the theory gives an adequate quantitative estimate of the energy stabilization of cyclopropenyl cation due to resonance or delocalization of the  $\pi$  electrons. The energy of reaction 1 is not a satisfactory measure of the resonance energy, since other  $C_3$  cations, which are nonaromatic, also have substantial stabilization as measured by comparable reaction energies. There is also a change of strain energy implied in (1) since a formally trigonal carbon in the cyclopropenyl cation is replaced by a formally tetrahedral carbon in cyclopropene. A better estimate of the resonance energy can be obtained from eq 2



which implies a comparison between three-membered rings with an equal number of trigonal and tetrahedral carbon atoms on both sides of the equation. Using previous results, the theoretical energy for this reaction is  $69.5$  kcal mol<sup>-1</sup>. (It is possible that the cyclopropyl cation is not a full local minimum on the 6-31G\* surface,<sup>6</sup> but the use of the structure obtained by constraining to  $C_{2v}$  symmetry should be adequate for this purpose.)

Another reaction which can be used to compare resonance in the cyclopropyl and allyl cations is (3). Again



using previous results, the 6-31G\* energy for this reaction is  $38.2$  kcal mol<sup>-1</sup>. Experimental heats of formation ( $256, 4.9, 66.6,$  and  $226$  kcal mol<sup>-1</sup>)<sup>3d,14</sup> for the four species in eq 3 lead to  $31$  kcal mol<sup>-1</sup>. This is larger than the value of  $18$  kcal mol<sup>-1</sup> given by Breslow and Groves,<sup>3b</sup> which was based on old data of the appearance potential of  $C_3H_3^+$  from cyclopropene and an approximate estimate of the  $pK_R^+$  of the

Table 11. Geometry of Cyclopropenyl Cation (I)

C-C	1.377
C-H	1.095

Table III. Geometry of the Propargyl Cation (II)

C <sub>1</sub> -C <sub>2</sub>	1.360	C <sub>3</sub> -H	1.091
C <sub>2</sub> -C <sub>3</sub>	1.214	HCH	117.8°
C <sub>1</sub> -H	1.109		

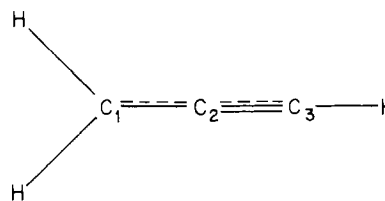
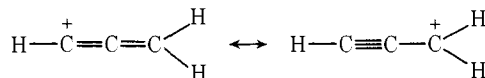


Figure 2. Propargyl cation (II).

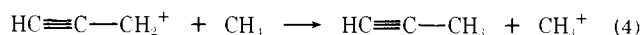
allyl cation. Actually, the energy from eq 3 is probably an underestimate of the resonance energy difference, since there is some relief of ring strain in this reaction. Combination of the energy from (3) with the resonance energy of allyl cation ( $\sim 26$  kcal mol<sup>-1</sup>, the ethyl stabilization energy)<sup>6</sup> again leads to an estimate of  $60$  kcal mol<sup>-1</sup> or greater for the resonance energy of the cyclopropenyl cation.

**Propargyl Cation (II).** The only other  $C_3H_3^+$  isomer which has a relatively low energy is the propargyl cation II (Figure 2). This structure has  $C_{2v}$  symmetry and can formally be derived by removing a hydride ion from either allene or propyne. The calculated carbon-carbon bond lengths (Table III) lie between those expected for the contributing resonance structures. The propargyl cation is calculated (6-31G\*) to be  $34.4$  kcal mol<sup>-1</sup> higher in energy



than the cyclopropenyl cation. This energy difference is somewhat higher than a recent experimental estimate ( $25$  kcal mol<sup>-1</sup>) obtained by Lossing.<sup>3d</sup>

Alternatively, we may estimate the heat of formation from the reaction



Use of previous data<sup>11</sup> gives  $31.2$  kcal mol<sup>-1</sup> for the 6-31G\* energy. Together with appropriate experimental heats of formation for  $\text{CH}_3^+$  and the neutral species ( $\Delta H_f^\circ$  (propyne) =  $46.3$  kcal mol<sup>-1</sup>),<sup>14</sup> we then obtain an estimate of  $293$  kcal mol<sup>-1</sup>. Using allene rather than propyne as a reference compound in (4) gives nearly the same results. This is again somewhat larger than the experimental estimate of  $281$  kcal mol<sup>-1</sup> due to Lossing.<sup>3d</sup>

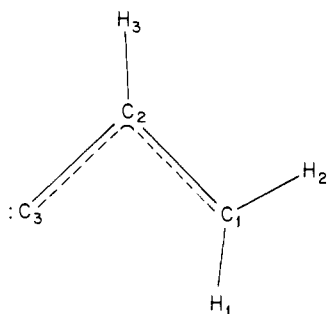


Figure 3. Prop-2-en-1-yl-3-ylidene cation (III).

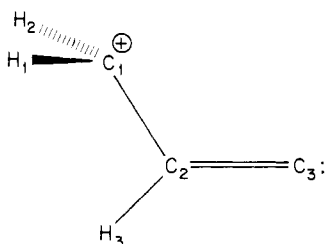
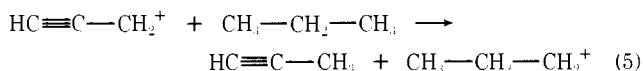


Figure 4. Perpendicular prop-2-en-1-yl-3-ylidene cation (IV).

Table IV. Geometry of Prop-2-en-1-yl-3-ylidene Cation (III)

C <sub>1</sub> -C <sub>2</sub>	1.377	C <sub>2</sub> C <sub>1</sub> H <sub>1</sub>	121.9°
C <sub>2</sub> -C <sub>3</sub>	1.396	C <sub>2</sub> C <sub>1</sub> H <sub>2</sub>	121.2°
C <sub>1</sub> -H <sub>1</sub>	1.102	C <sub>1</sub> C <sub>2</sub> H <sub>3</sub>	123.6°
C <sub>1</sub> -H <sub>2</sub>	1.102	C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	115.8°
C <sub>1</sub> -H <sub>3</sub>	1.090		

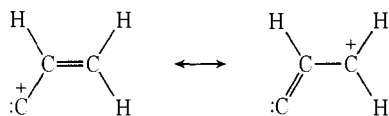
The energy of reaction 4 gives some measure of the additional stability of propargyl cation, that is, it gives the stabilization energy of an ethynyl substituent on a methyl cation. An alternative quantity is the stabilizing effect of an ethynyl relative to a saturated ethyl substituent so that comparison is made between systems with the same number of carbon atoms (eq 5). The 6-31G\* energy of this is  $-0.5$  kcal



$\text{mol}^{-1}$  which is remarkably small. This presumably reflects cancellation between stabilization due to  $\pi$ -electron conjugation in  $\text{HC}\equiv\text{C}-\text{CH}_2^+$  with the higher polarizability of the ethyl group in  $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2^+$ . Solvolytic studies also indicate that the propargyl systems do not show enhanced reactivity relative to acyclic models.<sup>15</sup>

The other  $\text{C}_3\text{H}_3^+$  species considered have much higher energies (Table I) and are not as likely to be found experimentally. While these species are minima within the symmetry constraints imposed, there is a possibility that they may only be saddle points on the full potential energy surface so that direct conversion without activation to I or II may occur.

**Prop-2-en-1-yl-3-ylidene Cation (III).** This cation (Figure 3) with  $C_s$  symmetry may be written as a resonance hybrid and accordingly may be named either prop-2-en-1-yl-1-ylidene or prop-2-en-1-yl-3-ylidene. It is closely related to the allyl cation from which it can be formally derived by abstraction of a pair of hydrogen atoms. The C-C bond lengths (Table IV) lie between those of normal single and



double bonds and are similar to those in the allyl cation (1.385 Å). There is some reduction in the CCC bond angle (115.8 vs. 118.9° in allyl).<sup>6</sup>

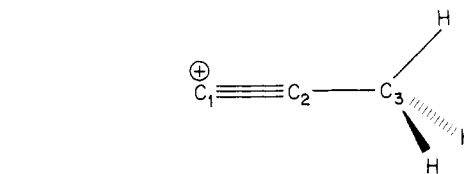


Figure 5. 1-Propynyl cation.

Table V. Geometry of Perpendicular Prop-2-en-1-yl-3-ylidene Cation (IV)

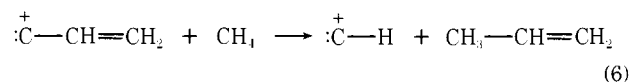
C <sub>1</sub> -C <sub>2</sub>	1.458	C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	131.0°
C <sub>2</sub> -C <sub>3</sub>	1.333	H <sub>1</sub> C <sub>1</sub> C <sub>2</sub>	116.3°
C <sub>1</sub> -H <sub>1</sub>	1.120	C <sub>2</sub> C <sub>1</sub> H <sub>1,2</sub>	177.7° <sup>a</sup>
C <sub>1</sub> -H <sub>3</sub>	1.100	C <sub>1</sub> C <sub>2</sub> H <sub>3</sub>	115.4°

<sup>a</sup> Throughout this paper, the notation  $H_{AB}$  is used to denote a point on the bisector of  $H_A\text{C}H_B$ .

Table VI. Geometry of the 1-Propynyl Cation (V)

C <sub>1</sub> -C <sub>2</sub>	1.394	C <sub>3</sub> -H	1.098
C <sub>2</sub> -C <sub>3</sub>	1.481	C <sub>2</sub> C <sub>3</sub> H	109.0°

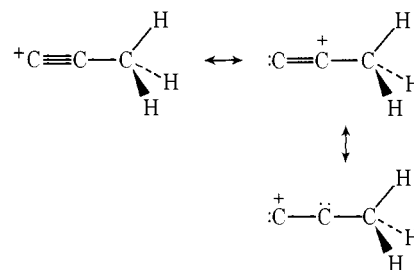
The energy of reaction 6 is of interest, being a measure of the stabilization of the monocoordinate cation  $\text{C}^+\text{H}$  by a



vinyl group. The theoretical result is  $76.1$  kcal  $\text{mol}^{-1}$  (6-31G\*). However, in spite of this fairly large stabilization, the total energy of III is  $35$  kcal  $\text{mol}^{-1}$  above that of the propargyl cation (II) by direct comparison of the energies in Table II.

**Perpendicular Prop-2-en-1-yl-3-ylidene Cation (IV).** Rotation of the terminal methylene groups in III through  $90^\circ$  gives the perpendicular prop-2-en-1-yl-3-ylidene cation (IV, Figure 4, Table V). In this structure, delocalization of the  $\pi$  electrons of the double bond into the vacant p orbital at  $\text{C}^+$  is no longer possible and the bonds may be distinctly recognized as single (1.458 Å) and double (1.333 Å), a result similar to that observed for the perpendicular allyl cation.<sup>6</sup> The energy of IV relative to III, i.e.,  $33.6$  kcal  $\text{mol}^{-1}$  (6-31G\*), represents the barrier to rotation of the methylene group and is very close to the corresponding figure for the allyl cation ( $34.8$  kcal  $\text{mol}^{-1}$  with 6-31G\*).<sup>6</sup>

**1-Propynyl Cation (V).** If the methine hydride ion of propyne is removed, the 1-propynyl cation (V, Figure 5) is obtained. This may alternatively be called the prop-1-en-2-yl-1-ylidene or propan-1-yl-1,2-diylidene cation because of the alternative resonance structures:



The theoretical geometry was determined imposing  $C_s$  symmetry but the best structure turned out to be close to  $C_{3v}$  symmetry (Table VI). The calculated  $\text{C}_1-\text{C}_2$  bond length is long (1.396 Å) and suggests contribution from the dicarbene structure above. The best wave function for this

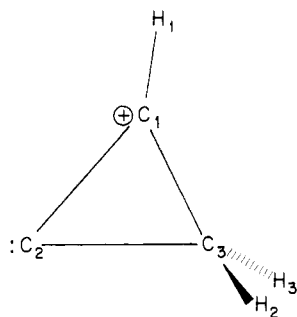


Figure 6. Cycloprop-1-yl-2-ylidene cation (VI).

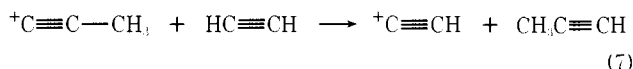
Table VII. Geometry of Cycloprop-1-yl-2-ylidene Cation (VI)

C <sub>1</sub> -C <sub>2</sub>	1.641	C <sub>3</sub> C <sub>1</sub> H <sub>1</sub>	145.1°
C <sub>2</sub> -C <sub>3</sub>	1.530	C <sub>1</sub> C <sub>3</sub> H <sub>23</sub>	144.7°
C <sub>1</sub> -C <sub>3</sub>	1.456	H <sub>2</sub> C <sub>3</sub> H <sub>3</sub>	110.7°
C <sub>1</sub> -H	1.109		
C <sub>3</sub> -H	1.104		

Table VIII. Geometry of Propan-1-yl-1,3-diyidene Cation (VII)

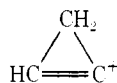
C <sub>1</sub> -C <sub>2</sub>	1.457	C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	106.0°
C <sub>2</sub> -C <sub>3</sub>	1.623	H <sub>1</sub> C <sub>2</sub> H <sub>2</sub>	109.6°
C <sub>3</sub> -H	1.104	C <sub>1</sub> C <sub>2</sub> H <sub>12</sub>	124.8°
C <sub>3</sub> -H	1.128	C <sub>2</sub> C <sub>3</sub> H <sub>3</sub>	99.1°

species involves complex molecular orbitals. The cation can be regarded as a methyl-substituted C<sub>2</sub>H<sup>+</sup>. The latter is predicted to have only two π electrons in its singlet ground state<sup>9</sup> and V has a similar electron configuration. The stabilization of the singlet ethynyl cation by the methyl substituent can be estimated from the energy of reaction 7. Actual-



ly, the ground state of C<sub>2</sub>H<sup>+</sup> is probably a triplet,<sup>9</sup> but no triplet structures of V were studied. This is 26.1 kcal mol<sup>-1</sup> (6-31G\*). However, the total energy of V is so far above I or II that it is likely to be very unstable.

**Cycloprop-1-yl-2-ylidene Cation (VI).** Abstraction of a pair of hydrogen atoms from the cyclopropyl cation leads to the cycloprop-1-yl-2-ylidene cation (VI, Figure 6). This cation is found to give a local minimum (within C<sub>s</sub> symmetry) corresponding to only two π electrons. The latter are mainly associated with the methylene group, so that the π atomic orbitals in C<sub>1</sub> and C<sub>2</sub> are relatively empty and the C<sub>1</sub>-C<sub>2</sub> bond is correspondingly long (1.641 Å, Table VII). We attempted to determine the geometry of the alternative structure with four π electrons, viz.,



but this was found to collapse to the propargyl cation II without activation. Since the two electron configurations lead to the same overall electronic symmetry, it seems unlikely that VI will exist as a cyclic species.

**Propan-1-yl-1,3-diyidene (VII).** The dicarbene cation, propan-1-yl-1,3-diyidene (VII, Figure 7), has a high relative energy. Its calculated structure (Table VIII) shows an even longer C<sub>2</sub>-C<sub>3</sub> bond (1.623 Å) than that calculated<sup>5</sup> for the 1-propyl cation (1.592 Å) reflecting strong hyperconjugation between the C<sub>2</sub>-C<sub>3</sub> bond and the formally vacant p orbital at C<sup>+</sup>. This is also responsible for the short C<sub>1</sub>-C<sub>2</sub> bond (1.457 Å).

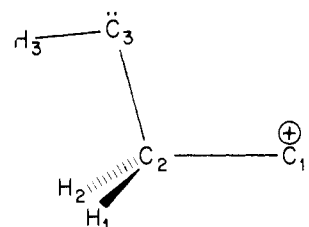


Figure 7. Propan-1-yl-1,3-diyidene cation (VII).

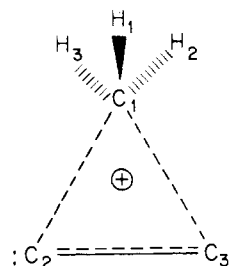


Figure 8. Corner protonated cyclopropyne (VIII).

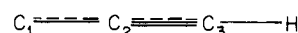


Figure 9. Propa-1,2-dien-1-yl-3-ylidene cation (IX).

Table IX. Geometry of Corner Protonated Cyclopropyne

C <sub>1</sub> -C <sub>2</sub>	1.819	H <sub>1</sub> C <sub>1</sub> pl <sup>a</sup>	73.4°
C <sub>2</sub> -C <sub>3</sub>	1.461	H <sub>23</sub> C <sub>1</sub> pl	52.7°
C <sub>1</sub> -H <sub>1</sub>	1.097	H <sub>2</sub> C <sub>1</sub> H <sub>3</sub>	107.6°
C <sub>1</sub> -H <sub>2</sub>	1.099		

<sup>a</sup> The notation H<sub>1</sub>C<sub>1</sub>pl is used to denote the angle between C<sub>1</sub>-H<sub>1</sub> and the plane of the ring

**Corner Protonated Cyclopropyne (VIII).** The final C<sub>3</sub>H<sub>3</sub><sup>+</sup> structure (VIII, Figure 8) may be formally named corner protonated cyclopropyne but, in fact, corresponds more closely to methylated :C=C:. The best wave function is complex. The long C-C bonds (1.819 Å, Table IX) are similar to other approximately one electron C-C bonds as, for example, in corner and edge protonated cyclopropanes.<sup>5</sup> It is also of interest to make comparison with protonated :C=C: where the C-H length (1.397 Å) is typical of one-electron C-H bonds and the C-C bond length (1.436 Å) is not too different from that found here for VIII. The energy of VIII relative to V (74 kcal mol<sup>-1</sup>, 4-31G) corresponds to the activation energy required for a 1,2-methyl shift in the 1-propynyl cation. This value is likely to be too high because the energies of cyclic relative to acyclic molecules are overestimated with the 4-31G basis. Nevertheless, it seems that the energy required for a 1,2-methyl shift increases as we proceed along the sequence 1-propyl (~0 kcal mol<sup>-1</sup>, 4-31G; -4 kcal mol<sup>-1</sup>, 6-31G\*),<sup>5</sup> 1-propenyl (18 kcal mol<sup>-1</sup>, 4-31G; 10 kcal mol<sup>-1</sup>, 6-31G\*),<sup>6</sup> 1-propynyl (74 kcal mol<sup>-1</sup>, 4-31G).

**C<sub>3</sub>H<sup>+</sup> Cations.** We have examined two acyclic structures for C<sub>3</sub>H<sup>+</sup> corresponding to protonation of neutral C<sub>3</sub> at a terminal carbon and on the central carbon, respectively. All attempts to locate minima corresponding to singlet cyclic isomers led to reopening without activation. The energies of the two structures found are listed in Table X.

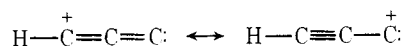
**Propa-1,2-dien-1-yl-3-ylidene Cation (IX).** The more stable form of C<sub>3</sub>H<sup>+</sup> (IX, Figure 9) may be formally derived from the propargyl cation (II) by removal of two hydrogen atoms. As with the propargyl cation, more than one resonance structure may be written for IX

Table X. Calculated Energies for C<sub>3</sub>H<sup>+</sup> Cations

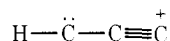
Cation	STO-3G		4-31G		6-31G* Total, hartrees
	Total, hartrees	Relative, kcal mol <sup>-1</sup>	Total, hartrees	Relative, kcal mol <sup>-1</sup>	
IX Propa-1,2-dien-1-yl-3-ylidene	-112.27535	0	-113.49373	0	-113.65222
X Prop-2-en-1-yl-1,3-diylidene	-112.21407	38.4	-113.42066	45.9	

Table XI. Geometry of Propa-1,2-dien-1-yl-3-ylidene Cation (IX)

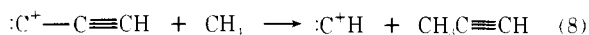
C <sub>1</sub> -C <sub>2</sub>	1.380	C <sub>3</sub> -H	1.102
C <sub>2</sub> -C <sub>3</sub>	1.213		



leading to the possible names, propa-1,2-dien-1-yl-3-ylidene and prop-2-yn-1-yl-1-ylidene. The theoretical structure (Table XI) is found to be linear with C<sub>∞v</sub> symmetry. The bond lengths correspond more closely to the second structure and are close to those found for the propargyl cation. The fact that the C<sub>1</sub>-C<sub>2</sub> bond length is slightly longer than in propargyl seems to imply that the contribution from an additional resonance structure must be relatively small.



We may attempt to estimate the heat of formation of IX by treating it as a monocoordinate cation substituted by ethynyl. Thus, from the theoretical energy of reaction 8



(55.5 kcal mol<sup>-1</sup> at 6-31G\*) and experimental heats of formation for the other species, we calculated a heat of formation of 406 kcal mol<sup>-1</sup>. Experimental estimates<sup>2</sup> range from 280 to 360 kcal mol<sup>-1</sup>. This rather large discrepancy suggests that we may not yet have found the most stable form for C<sub>3</sub>H<sup>+</sup>. The stabilization energy found for reaction 8 seems consistent with the value (76 kcal mol<sup>-1</sup>) found for the vinyl substituent (reaction 6). It does seem likely, therefore, that IX has a heat of formation considerably higher than the reported experimental heats of formation of C<sub>3</sub>H<sup>+</sup>.

**Prop-2-en-1-yl-1,3-diylidene Cation (X).** The second C<sub>3</sub>H<sup>+</sup> structure we have studied (X, Figure 10) with C<sub>2v</sub> symmetry may be formally derived from the allyl cation by abstraction of four hydrogen atoms, or from III by abstraction of two hydrogen atoms. It is also stabilized by charge delocalization and this is reflected in the C=C bond lengths (1.387 Å, Table XII). The energy difference between IX and X is 45.9 kcal mol<sup>-1</sup> (4-31G) so that X is likely to be quite unstable.

## Conclusion

The cyclopropenium ion (I), indicated to have resonance energy exceeding 60 kcal mol<sup>-1</sup>, is the most stable C<sub>3</sub>H<sub>3</sub><sup>+</sup> cation. The propargyl cation II, 34 kcal mol<sup>-1</sup> less stable than I, is the only other energetically reasonable alternative. The ethynyl group in II does not stabilize the primary carbocation to any greater extent than does an ethyl group. This contrasts with the large stabilization provided by the vinyl group in the allyl cation.

All of the C<sub>3</sub>H<sup>+</sup> species examined were indicated to be quite high in energy. The most stable structure for C<sub>3</sub>H<sup>+</sup> found in this study is linear. However, a large discrepancy

Table XII. Geometry of Prop-2-en-1-yl-1,3-diylidene Cation (X)

C <sub>1</sub> -C <sub>2</sub>	1.387	C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	123.9°
C <sub>2</sub> -H	1.101		

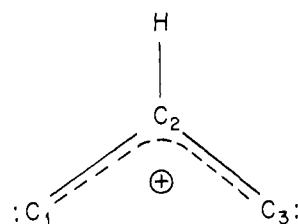


Figure 10. Prop-2-en-1-yl-1,3-diylidene cation (X).

exists between the experimental heats of formation for C<sub>3</sub>H<sup>+</sup> and our theoretical value.

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