ometry calculations lead to an artificial restriction of the available conformational-phase space and an overestimation of rotational barriers.[43] However, unlike adiabatic mapping, the filtered structures along a trajectory correspond to average structures due to high-frequency vibrations and not the structures corresponding to the lowest energy. In other words, adiabatic mapping yields idealized "zero temperature" structures whereas the filtered trajectory results in realistic "effective" transient structures. When combined with filtering of the corresponding energy trajectories,[24] this technique can provide unique information about structural and energetic changes during conformational transitions.

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The Nature of Doubly Charged $C_3H_4^{2+}$ Ions: Structural and Energetic Relationships

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Abstract: The singlet and triplet allene dications prevail on the $C_3H_4^{2+}$ potential hypersurface at higher levels of ab initio theory. The global minimum, the planar allene dication **1**, lies in a deep potential well with a deprotonation barrier of 82 kcal/mol. This dication has similar barriers of ca. 15 kcal/mol for scrambling of both its hydrogens and carbons. The existence of a protonated cyclopropenium ion is unlikely. The triplet propyne dication, the least stable isomer studied, is ca. 14 kcal/mol higher in energy than the perpendicular triplet allene dication and is ca. 54 kcal/mol less stable than the planar singlet global minimum **1**.

This paper is concerned with the $C_3H_4^{2+}$ potential energy surface. The isomers **1–10**, studied at reasonably high levels of ab initio theory, reveal unusual structural features and are related to several problems of interest: the nature of $C_3H_4^{2+}$ ions generated in the gas phase, the preference for anti van't Hoff geometries (e.g., for planar tetracoordinate carbons),[1] and the mechanism of the electrophilic substitution of aromatic cyclopropenium ions.[2]

Organic dications are now common in the gas phase, but only some energetic and structural information is available experimentally.[3] Hence, there is an increasing number of theoretical studies of such species: those dealing with the $C_nH_4^{2+}$ series (n = 1, 2, 4, 5, and 6) are most pertinent to the present work.[4]

Although $C_3H_4^{2+}$ ions have been generated by electron impact,[5] by charge exchange,[6] and by charge stripping,[7] no detailed gas-phase data are available. Franklin and Mogenis[5a] reported the observation of $C_3H_4^{2+}$ by electron impact on allene in 1967; ΔH_f° = 743 kcal/mol was estimated from the appearance potential. This value appears to be much too high (heats of formation nearer 600 kcal/mol are to be expected). Proton ejection from $C_3H_4^{2+}$ was observed to be the most likely decomposition pathway.[5a] From the 3.24 Å intercharge distance for this process, calculated from the 4.44 eV kinetic energy released in the charge separation experiment, March suggested $C_3H_4^{2+}$ to have a cyclic structure.[7c] In the present study we show this proposal to be very unlikely. As has been recognized in the literature,[4,8] doubly ionized allene should have a planar singlet ground state **1**; the D_{2d} form **2** as well as the propyne dication **3** should be triplets.

The cyclopropenium ion has twice the resonance energy of benzene.[9] The traditional chemical reaction characteristic of aromatic molecules is their ability to undergo electrophilic substitution, rather than addition. Indeed, H^+/D^+ exchange has been reported experimentally for a cyclopropenium ion with stabilizing substituents.[10] Stimulated by this result, Clark and Weiss[11] investigated such electrophilic substitution reactions of cyclopropenium ions calculationally. Geometries were optimized with the minimal STO-3G basis set, and the final energies were obtained at the split valence 4-31G ab initio level. Several intriguing results for the parent $C_3H_4^{2+}$ species were reported. Among the cyclic isomers (**7–10**), a form **7** with a planar tetracoordinate carbon was found to have the lowest energy. The edge protonated **8**, second in stability, was considerably better than the corner

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Table I. Total Energies (au) of $C_3H_4^{2+}$, $C_3H_3^+$, and C_3H_4 Isomers

					6-31G**//MP2/6-31G*[a]			
structure	symm	HF/3-21G	HF/6-31G*	MP2/6-31G*	HF	MP2	MP3	MP4
1	D_{2h}	114.346 57	114.997 28	115.321 62	115.004 96	115.333 98	115.363 75	115.385 26
2[b]	D_{2d}	114.304 93	114.966 83	115.258 07[c]	114.974 19	115.271 58	115.307 62	115.322 01
3[b]	C_{3v}	114.252 61	114.914 35	115.234 28[d]	114.920 88	115.246 40	115.275 41	115.295 60
4	C_s	114.191 66	114.834 04	115.195 04	114.838 82	115.201 56	115.217 37	115.247 86
5	C_s	114.313 97	114.968 18	115.291 92	114.966 64	115.304 84	115.333 62	115.355 33
6	C_s	114.288 19	114.957 28	115.302 21	114.967 40	115.317 44	115.341 38	115.364 13
7	C_{2v}	114.259 20	114.947 53	115.309 03	114.953 63	115.320 43	115.340 64	115.362 16
8	C_{2v}	114.241 03	114.943 27	115.306 30	114.954 65	115.321 96	115.341 84	115.363 06
9	C_{2v}	114.233 99	114.907 03	115.263 19	114.918 56	115.280 76	115.302 98	115.322 95
10	C_{3v}	114.215 62	114.913 75	115.259 28	114.926 98	115.276 41	115.301 91	115.319 83
cyclopropenium ion	D_{3h}	114.329 57	115.007 02		115.013 29	115.369 37	115.390 35	115.407 99
propargyl ion	C_{2v}	114.309 49	114.951 00		114.956 89	115.316 85	115.336 34	115.362 14
propyne	C_{3v}	115.225 39	115.864 32		115.871 25	116.270 29	116.291 96	116.314 38
allene	D_{2d}	115.219 91	115.861 10		115.868 55	116.264 91	116.291 34	116.312 49
cyclopropene	C_{2v}	115.162 01	115.823 05		115.830 53	116.236 29	116.259 41	116.279 29

[a] HF/6-31G* optimized geometries were used for the monocations and neutral hydrocarbons. [b] Triplet structures. UHF and UMP values were used. [c] $\langle s^2 \rangle = 2.01$. [d] $\langle s^2 \rangle = 2.02$.

Table II. Relative Energies (kcal/mol) of $C_3H_4^{2+}$ and $C_3H_3^+$ Isomers

						6-31G**//MP2/6-31G*[d]				
structure	symm	HF/4-31G[a]	HF/3-21G[c] [ZPE]	HF/6-31G*	MP2/6-31G*[c] [ZPE]	HF	MP2	MP3	MP4	+ZPE
1	D_{2h}		0.0 (0) [34.3]	0.0	0.0 (0) [32.1]	0.0	0.0	0.0	0.0	0.0
2[e]	D_{2d}		26.1 (0) [34.6]	19.1	39.9	19.3	39.2	35.2	39.7	40.0*
3[e]	C_{3v}		59.0 (0) [31.2]	52.0	54.8	52.8	55.0	55.4	56.3	53.5*
4	C_s		97.2 (1) [29.2]	102.4	79.4	104.3	83.1	91.9	86.2	81.6*
5	C_s	0.0	20.5 (0) [35.0]	18.3	18.6 (1) [33.0]	24.0	18.3	18.9	18.8	19.7*
6	C_s		36.6 (1) [32.2]	25.1	12.2 (0) [31.8]	23.6	10.4	14.0	13.3	13.0
7	C_{2v}	31.9	54.8 (1) [32.5]	31.2	7.9 (0) [32.0]	32.2	8.5	14.5	14.5	14.4
8	C_{2v}	42.8	66.2 (1) [32.9]	33.9	9.6 (0) [32.8]	31.6	7.5	13.7	13.9	14.6
9	C_{2v}	49.0	70.6 (0) [31.9]	56.6	36.7 (1) [30.9]	22.8	33.4	38.1	39.1	38.0
10	C_{3v}	62.5	82.2 (2) [31.1]	52.4	39.1 (2) [29.9]	48.9	36.1	38.8	41.1	39.0
cyclopropenium ion	D_{3h}		10.7	-6.1		-4.6	-22.5	-16.8	-14.5	
propargyl ion	C_{2v}		23.3	29.0		30.8	10.5	17.1	14.3	

[a] From ref 11, STO-3G geometry. [b] HF/6-31G* optimized geometries were used for the monocations. [c] Values in parentheses refer to the number of imaginary frequencies. The values in brackets are the unscaled zero-point energies. [d] Where available MP2/6-31G* ZPE corrections were used, scaled by 0.95. Where not available (indicated by an asterisk HF/3-21G ZPE corrections were used, scaled by 0.9. [e] Triplet structures. UHF and UMP values were used.

protonated **9** corresponding to the benzenonium ion (protonated benzene). This species **9** might also arise from the vertical double ionization of cyclopropene. However, a ring opened geometry **5** was indicated to be energetically more stable than any of these alternatives.

In the ensuing years since Clark and Weiss' paper[11] there have been notable advances both in computer technology and in the efficiency and scope of quantum mechanical programs. This now allows deficiencies, recognized in the 1980 study, to be overcome. In particular, both polarized basis sets (e.g. 6-31G* and 6-31G**) and electron correlation (e.g. at the MP4SDTQ level) are expected to favor three-membered rings and delocalized, aromatic structures preferentially.[12] As part of our general study of carbodications,[13] we have now extended the work of Clark and Weiss and have also examined the allene ($H_2CCCH_2^{2+}$, **1** (D_{2h}) and **2** (D_{2d})) and propyne-related (H_3CCCH^{2+}, **3** (C_{3v})) geometries (which were outside the scope of the earlier study), as well as transition structures for proton loss and isomerizations. Relationships in the $C_nH_4^{2+}$ series are deduced. For this purpose, comparisons with the CH_4^{2+}, $C_2H_4^{2+}$, $C_4H_4^{2+}$, as well as $C_5H_4^{2+}$, as well as $C_5H_4^{2+}$ and $C_6H_4^{2+}$ systems, reported earlier,[13] are given. For example, linear isomers with the general formula $H_2(C)_nH_2^{2+}$ favor "anti van't Hoff" geometries. This present high-level study on $C_3H_4^{2+}$ isomers confirms this expectation. We show that the branched and cyclic forms (**5**–**10**) studied by Clark and Weiss, while not much higher in energy than the allene dication **1**, are not likely to survive rearrangement into the global minimum.

Methods

Pople's GAUSSIAN 82 and 88 programs[14] with the standard basis sets and correlation methods were employed.[15] The geometries were first optimized with the split-valence 3-21G basis set,[16a] which, as expected, gave relative energies comparable to the 4-31G//STO-3G results of Clark and

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Table III. Relative Energies (kcal/mol) of C_3H_4, $C_3H_4^{\cdot+}$ Isomers

	6-31G**					exp C_3H_4[a]		exp $C_3H_4^{\cdot+}$[b]	
geometry	HF	MP2	MP3	MP4	MP4[c]	ΔH_f°	ΔE	ΔH_f°	ΔE
propyne	0.0	0.0	0.0	0.0	0.0	44.4	0.0	283.7	0.0
allene	1.7	3.7	0.4	1.2	0.8	45.6	1.2	269.4	-14.3
cyclopropene	25.5	21.6	20.4	22.0	22.4	66.2	21.8	289.2	5.5

[a] Experimental heats of formation from ref 21d. [b] Experimental heats of formation from ref 23. [c] Scaled zero-point vibrational energies[31] corrected values.

Weiss.[11] The geometries of all ten $C_3H_4^{2+}$ isomers were next optimized with the heavy-atom polarized 6-31G* basis set.[16b] As will be discussed below, electron correlation corrections as well as polarization functions on carbon have a much larger effect on the relative energies, particularly when cyclic and open structures are compared. Therefore, the dication isomers were optimized at MP2/6-31G*. Key MP2 and HF/6-31G* (in parentheses) geometrical details are provided in structures displayed throughout the text; the correlated geometrical parameters are used in the text unless stated otherwise. The MP2/6-31G* geometries were then employed for single-point MP4SDTQ/6-31G** energy evaluations, using Møller–Plesset perturbation theory to the full fourth order.[17] The 6-31G** basis set[16b] includes p-type polarization functions on hydrogen. This is known to improve the description of H-bridged species.[15] Table I summarizes the absolute energies and Table II the relative energies, which are also displayed graphically in Figure 1. Table II also includes the zero-point vibrational energies (ZPE) calculated for **1**–**10** at the HF/3-21G level by analytical evaluation of the frequencies. At this level **1**, **2**, **3**, **5**, and **9** are found to be minima, whereas **4**, **6**, **7**, and **8** are transition structures with one negative eigenvalue in the Hessian matrix. However, this characterization of structures is misleading as is in fact suggested by some reversals of relative energies at the correlated levels (Table II and Figure 1). Hence, correlated frequency runs at MP2/6-31G* were used to establish the nature of the stationary points more precisely for some of the C_3H_4 isomers. At this level of theory **1**, **6**, **7**, and **8** are equilibrium structures, and **5** and **9** represent transition structures. The C_{3v} structure **10** has an interesting four-center–two-electron bonding arrangement, but it was found to be a saddle point of second order with two imaginary frequencies at both HF/3-21G and MP2/6-31G*. The "final" relative energies in Table II include corrections for scaled zero-point energy contributions. Where available, MP2/6-31G* ZPE values (scaling factor 0.95) are used; otherwise ZPE corrections were made with 0.9 scaled HF/3-21G values.

Results and Discussion

The Relative Energies of C_3H_4, $C_3H_4^+$, and $C_3H_3^+$ Isomers. To set the stage for the following discussion on $C_3H_4^{2+}$ dications, the relative energies of cyclic vs open isomers of C_3H_4, $C_3H_4^+$, and $C_3H_3^+$ provide calibration. Complete MP4SDTQ/6-31G**//HF/6-31G* + scaled[19] ZPE absolute energies for $C_3H_3^+$ and C_3H_4 are provided in Table I and their relative energies (along with experimental values) in Tables II and III, respectively. These results extend earlier data[12,20a,b] on these systems and, as can be seen, compare well with experiment.[21]

Of the C_3H_4 isomers, allene and propyne have nearly the same energy, whereas cyclopropene is 22 kcal/mol higher in energy. This reflects the high degree of strain in this small ring molecule which incorporates two formal sp^2 centers uncomfortably. The strain in the cyclopropenium ion must be even higher, since three formal sp^2 centers are now present in a three-membered ring. Nevertheless, the cyclopropenium ion is considerably lower in energy (29 kcal/mol) than the propargyl cation, $HC{\equiv}CCH_2^+$, despite the conjugated nature in the latter. This unusual stability of the cyclopropenium ion is due to the very large 2π aromatic resonance, which can be evaluated by means of eq 1; at MP2/6-31G** the stabilization energy is 71.0 kcal/mol.[9] Consequences of this aromaticity will be discussed further below.

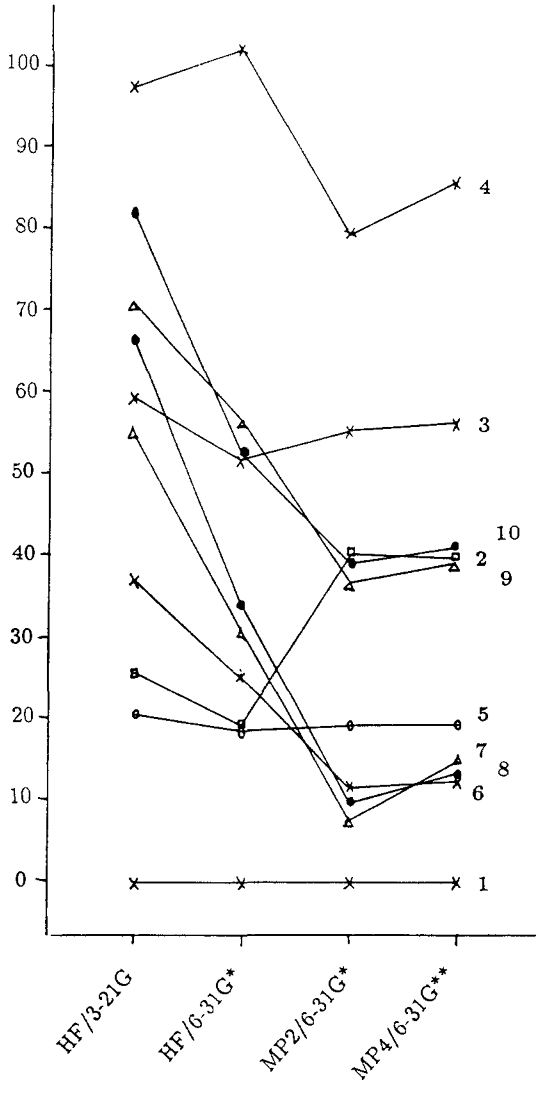

Figure 1. Plot of relative energies (kcal/mol) vs basis set. All energies are relative to **1**.

$$c\text{-}C_3H_6 + c\text{-}C_3H_3^+ \rightarrow c\text{-}C_3H_5^+ + c\text{-}C_3H_4 \qquad (1)$$

Although not calculated in the present work,[22] the experimentally available relative energies of $C_3H_4^{\cdot+}$ radical cations are included in Table III.[23] The cyclopropene radical cation, which

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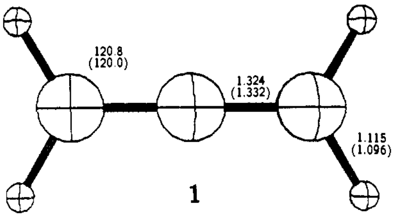
does not benefit from aromatic resonance, remains some 20 kcal/mol higher in energy than the allene radical cation, although the difference with regard to the propyne radical cation (5 kcal/mol) has become substantially less. Removal of a second electron from these $C_3H_4^{\cdot+}$ systems to give $C_3H_4^{2+}$ results in a different ordering, as is discussed below.

Dication Stabilities. The relative $C_3H_4^{2+}$ energies, displayed in Figure 1, demonstrate the very strong dependence both on the basis set, in particular the effect of carbon polarization, and on electron correlation. For example, the 45.7 kcal/mol energy difference between **8** and **5** at HF/3-21G reduces to 12.9 kcal/mol at HF/6-31G* and reverses sign to −1.0 kcal/mol at MP4/6-31G**. The effects are well recognized: carbon d-polarization functions are required for the structural and energetic description of small cyclic systems, and electron correlation corrections stabilize bridging and aromatic systems preferentially.[15] In the present case the energies of structures **5–8** become nearly the same. As expected, the related energy of the triplet planar allene dication **2** is higher at electron correlated levels.



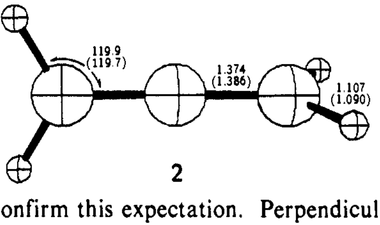
1

The stability of the $C_3H_4^{2+}$ global minimum, dication **1**, can be assessed by estimating its heat of formation. Using the calculated heats of reactions 2 and 3 and experimental heats of formation $\Delta H_f°(298)$ for the fragments,[21] i.e., 367 kcal/mol for H^+, 261 kcal/mol for CH_3^+, 17.9 kcal/mol for CH_4, 256 kcal/mol for $C_3H_3^+$, and 226 kcal/mol for $C_3H_5^+$, gives estimated heats of formation of 641.3 and 643.8 kcal/mol, respectively.

$$C_3H_4^{2+} \rightarrow C_3H_3^+ + H^+ \quad +18.3 \text{ kcal/mol (MP4/6-31G**+ZPE)} \tag{2}$$

$$C_3H_4^{2+} + CH_4 \rightarrow C_3H_5^+ + CH_3^+ \quad +138.9 \text{ kcal/mol (MP4/6-31G**+ZPE)} \tag{3}$$

Linear Isomers 1–4. As expected from qualitative considerations, the singlet allene dication **1** should prefer a planar D_{2h} structure in contrast to allene itself which has perpendicular D_{2d} symmetry. Since the π-HOMO's of allene are degenerate, its dication in D_{2d} symmetry should have a triplet ground state (**2**).

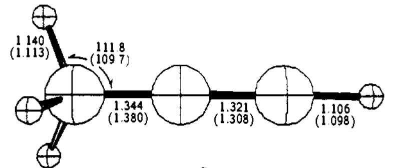


2

Our results confirm this expectation. Perpendicular **2** has one electron each in the two orthogonal π-systems; further stabilization due to the hyperconjugative interaction with the terminal CH_2 groups is present. However, the final relative energy of **2** is nearly 40 kcal/mol above that of **1**. This difference may be taken as an approximate measure of the rotational barrier of the allene dication which thus is nearly as large as the rotational barrier in allene itself (51.3 kcal/mol, MP3/6-31G*).[20] This emphasizes that anti van't Hoff dication structures are nearly as favorable as their neutral van't Hoff cumulene counterparts.

The electronic structure of **1** is particularly favorable. The 2π electrons are delocalized in an allyl cation-like arrangement. The formally vacant p-orbital on the central carbon in the orthogonal plane interacts hyperconjugatively with both CH_2 groups; this is reflected in its short C–C bonds of 1.324 Å. The C–C bonds in perpendicular **2** are 0.050 Å longer.

The hyperconjugative stabilization in the linear propyne dication **3** evidently is less; the C–C bond lengths are 1.321 and 1.344 Å. This triplet species, the methyl derivative of the acetylene dication, is 54 kcal/mol less stable than **1**, in part due to less effective charge distribution in the orthogonal degenerate π-SOMO's.

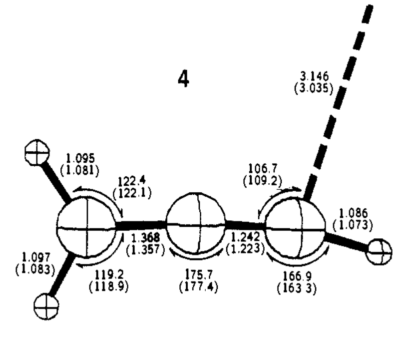


3

The accommodation of the two positive charges even in systems as small as He_2^{2+} [24] and CH_4^{2+},[13a,25] despite the large Coulombic repulsion, is due to the relatively high fragmentation barriers. Electrostatic repulsion also is responsible for the fact that **1** is the $C_3H_4^{2+}$ global minimum. As is revealed by population analyses (e.g., NBO/NLMO),[26] most of the positive charge in **1–10** resides on the hydrogens, rather than on the carbons. As a consequence, Coulomb repulsion is minimized when the hydrogens are as far apart as possible, as in the linear isomer **1**. This helps explain why **1** is more stable than the bent isomer **6** (which has a bridging hydrogen) as well as the cyclic isomers **7–10**, which, like $C_3H_3^+$, must benefit from considerable aromatic stabilization. However, linear cumulene dications are no longer the global $H_2C_nH_2^{2+}$ minima for n = 4–6.[13h,k] In each case, 2π-electron aromatic structures are lower in energy.

Allene dication **1** has significant kinetic stability toward deprotonation (**4**) to the linear propargyl cation. The barrier for this 14.3 kcal/mol endothermic process is 86.2 kcal/mol (MP4/6-31G**). As in related cases, the C–H distance to the departing proton in the transition structure **4** is quite long, i.e., 3.146 Å. Such long dissociating C–H bonds are rather common,[27] since most carbodications have high barriers for deprotonation.[13] Because other fragmentation modes for **1** (e.g., loss of H_3^+, $H_2^{\cdot+}$, CH_3^+, etc.) are less favorable energetically, isomer **1** should be the most likely candidate for the readily observable gas-phase $C_3H_4^{2+}$ species.

4



The calculated adiabatic dioxidation from allene is 25.2 eV (MP4/6-31G**). A similar value of 25.5 eV is calculated from the heats of formation of allene and its dication, which are 45.6 and 642.6 (average value, see above) kcal/mol, respectively. However, the measured appearence potential for $C_3H_4^{2+}$ generated from allene is much larger. The experimental value of 30.2 eV, reported in an EI study,[5a] appears to be too large even for a vertical double ionization process. The value of 15.8 eV for the adiatic second ionization potential IE_a of allene, estimated from the radical cation and (singlet) dication heats of formation, is also significantly smaller than the Q_{min} of 17.3 eV determined from charge-stripping experiments.[28] However, this Q_{min} value is in excellent agreement

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(24) (a) Pauling L. *J. Chem. Phys.* **1933**, *1*, 56. (b) Guilhaus, M.; Brenton, A. G.; Beynon, J. H.; Rabrenović, M.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1985**, 210; *J. Phys. B* **1984**, *17*, L605.

(25) Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 1155.

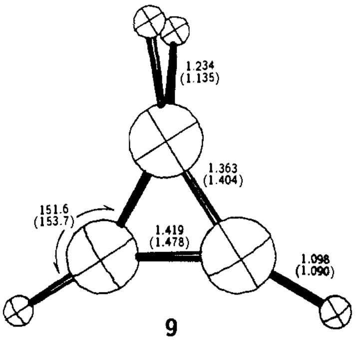
(26) (a) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *Ibid.* **1985**, *83*, 735. (c) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.

(27) Gill, P. M. W.; Radom, L. *Chem. Phys. Lett.* **1987**, *136*, 294.

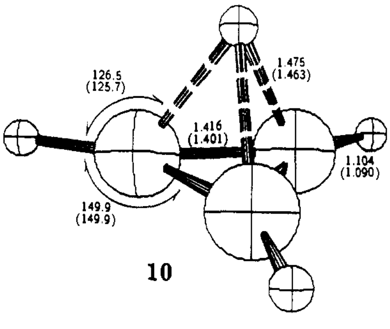
(28) Rabrenović, M.; Proctor, C. J.; Ast, T.; Herbert, C. G.; Brenton, A. G.; Beynon, J. H. *J. Phys. Chem.* **1983**, *87*, 3305.

with the calculated IE_a of 17.5 eV for the formation of triplet **2**.

Cyclic and Bent Isomers 5–10. As noted before by Clark and Weiss,[11] protonation of the cyclopropenium ion might occur at a corner (**7** or **9**), at an edge (**8**), or on a face (**10**). Interestingly, the "classical" isomer **9**, although corresponding to the most favorable form of protonated benzene (the Wheland intermediate), is one of the least stable $C_3H_4^{2+}$ structures among those investigated. Comparison of the HF and MP2/6-31G* geometrical parameters emphasizes that the formally localized, highly repulsive, positive charges on adjacent carbons are significantly stabilized through hyperconjugative interaction with the CH_2 group, to render at the correlated level a condensed cyclic C_3H_2 dication to which a H_2 molecule is complexed. Presumably because of the small size of the hydrogen 1s orbital, the four-center–two-electron (interstitial) bonding[29] in the C_{3v} face-protonated isomer **10** is not effective. In addition, the compact geometry of **10** results in rather strong Coulombic repulsion among the hydrogens, which bear most of the positive charges.



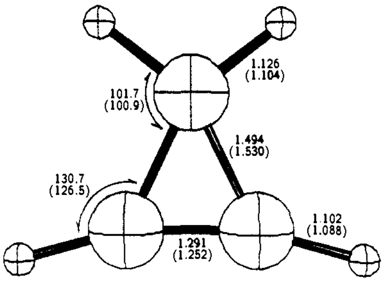
9



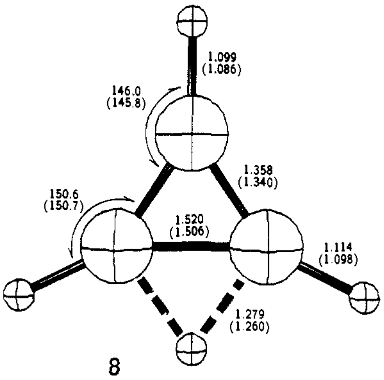
10

We are thus left with two candidates for the protonated cyclopropenium ion, **7** and **8**, which are both minima at the MP2/6-31G* level of theory. The relative energies of these two forms at polarized and at correlated levels differ very little, and our "final" ZPE corrected level favors the corner-protonated over the edge-protonated form by 0.2 kcal/mol. Thus, the protonated cyclopropenium ion is indicated to be a fluctional molecule with the hydrogens circulating rapidly in the plane around the carbons.

Clark and Weiss[11] found **5**, with an opened (or bent) structure, to be considerably more stable at 4-31G//STO-3G than any of the cyclic forms (**7**–**10**). This suggested that protonation of the cyclopropenium ion might lead to ring opening. Our 3-21G//3-21G results (Table I), confirming **5** to be a local minimum at this level, are similar to theirs, but this is also misleading. Inclusion of polarization functions significantly reduces the energy difference between **5** and its isomers **7** and **8** and after inclusion of electron correlation corrections **5** becomes the least stable of the three (Figure 1). The geometry of **5** as well as its character are also affected by the level of theory. While the geometry of **5** represents an open structure at the HF levels a more contracted geometry results at MP2/6-31G* (∠CCC = 100.6°). In fact, at the correlated level **5** represents the transition structure for ring opening of **7**, which is a process that requires 5.0 kcal/mol (MP4/6-31G**+ZPE).



7



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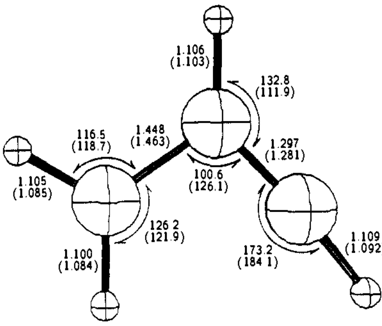
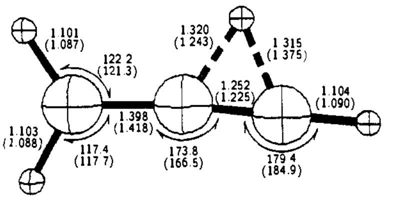


5

While **5** does not represent a local C_3H_4 minimum, structure **6** does; all eigenvalues of the MP2/6-31G* force constant matrix are positive. Its energy difference with **5** is 6.4 kcal/mol, and that with **1** amounts to 13.0 kcal/mol. While structure **1** is effectively stabilized by crosshyperconjugation (i.e. the combined conjugative stabilization in two orthogonal planes), the stabilization in **6** is smaller and reminiscent of the vinyl cation. It is well-known that at correlated levels the cyclic vinyl cation is more stable than the classical open structure. Apparently, this is also the case in dication **6** (a transition structure at HF/3-21G), which contains a bridging hydrogen and represents a CH_2^+-substituted vinyl cation. Although no transition from **6** to **1** was determined, it is expected that such a process has only a marginal barrier, giving virtually no kinetic stability to **6**. Also the kinetic stability for **8** is expected to be minimal.



6

Even though cyclic forms of the C_3H_4 dication have been characterized as local minima at correlated levels, transformation to the allene dication **1** will be extremely facile because of the

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[29] Bremer, M.; Schleyer, P. v. R.; Schoetz, K.; Kausch, M.; Schindler, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 761.

low barriers involved. This has the interesting consequence that H- and C-scrambling in dication **1** occurs in the same energy domain, i.e., ca. 15 kcal/mol (MP4/6-31G**) above **1**.

Comparisons with Other $C_nH_4^{2+}$ Dications. From our theoretical studies on carbodications with four hydrogens, $C_nH_4^{2+}$ (n = 1-6),[13a,e,h,k] ubiquous species in various types of mass spectroscopy,[3] some generalizations emerge:

1. Cumulene dications are minima for all $C_nH_4^{2+}$ dications and the global minima for the smaller members of the family, i.e., $n < 4$.[13a,e]

2. Structures that benefit from aromatic stabilization are favored for systems with more than 3 carbons.[13h,k] These dications disperse the charges better over the molecular framework than is the case with their linear conjugated isomers.

3. All energetically preferred dications have anti van't Hoff stereochemistry, except the cyclobutadiene dication,[13h,l] which enjoys a special type of aromatic stabilization. Illustrative examples are diionized methane, ethylene, propene, and cumulenes in general as well as structures containing three-membered rings, like the vinylidenecyclopropenium and trifulvalene dications.[4] Isomers **1** and **7** are explicit examples of the present study. The two-electron differences between dications and their neutral homologues underlie the reversal of the van't Hoff rule.

4. The methyl-substituted acetylenic-like dications, $CH_3C_nH^{2+}$, are the least favored isomers for all $C_nH_4^{2+}$ dications. Hence, the suggestion in the mass spectroscopic literature[3d] that these species share this common structure is incorrect.

5. All $C_nH_4^{2+}$ species are more compact than the corresponding neutral hydrocarbons. In most cases this results from effective types of hyperconjugation, which also reduces the electrostatic repulsion of charges.

6. All $C_nH_4^{2+}$ dications have significant kinetic stability. Barriers for proton loss steadily increase from the methane dication up to the larger cumulenic-type dications for which such processes become even endothermic. These values, followed by the endothermicities for proton loss (all in kcal/mol), are for CH_4^{2+} 17 and −106,[13a] for $C_2H_4^{2+}$ 16 and −65,[13e] for $C_3H_4^{2+}$ 82 and 11, for $C_4H_4^{2+}$ (D_{2d}) 120 and 54 (3-21G), and for linear $C_5H_4^{2+}$ (D_{2h}) 128 and 71 (3-21G) kcal/mol.[30] Consequently, disproportionation of larger dications gives preferentially larger fragments. As is the case in **4**, the proton dissociates at large distances (i.e., 3.257 Å for $C_4H_4^{2+}$ (D_{2d}) and 3.488 Å for $C_5H_4^{2+}$ (D_{2d})),[30] conforming to the Hammond principle.

Conclusions. The important points deduced from the present study are the following: 1. The allene dication **1** is the singlet global $C_3H_4^{2+}$ minimum. Structures representing hydrogen and carbon scrambling are about 15 kcal/mol less stable at MP4/6-31G**. 2. It appears that all protonated cyclopropenium ion forms will convert to the allene dication with very small barriers. 3. Although the triplet surface was not searched explicitly, the perpendicular allene dication is a minimum, albeit ca. 40 kcal/mol less stable than the planar singlet form. 4. Whereas propyne is the most stable neutral C_3H_4 hydrocarbon isomer and its radical cation is observable in the gas phase, the (triplet) dication is the highest energy form of the $C_3H_4^{2+}$ species studied. 5. The deprotonation barrier of the $C_3H_4^{2+}$ dication is 82 kcal/mol. This process is endothermic by 11 kcal/mol (MP4/6-31G**+ZPE).

Acknowledgment. We thank the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Alabama Supercomputer Center for support of this work in Alabama and, in Erlangen, the Funds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, the Volkswagenstiftung, and the Convex Computer Corp. This study benefited from a Deutsche Academische Austausch Dienst study grant to K.L. One of the referees is thanked for valuable comments.

Note Added in Proof. Since this work was submitted, we became aware of a study on the potential energy surface of $C_3H_4^{2+}$: Wong, M. W.; Radom, L. *J. Mol. Struct.* **1989**, *198*, 391. Our dication results are in agreement with their study.

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[30] The 3-21G energies for $C_4H_4^{2+}$ (D_{2d}) and $C_5H_4^{2+}$ (D_{2d}) are 152.033 14 and 189.699 30 au, respectively, and for the corresponding transition structures for deprotonation 151.841 51 and 189.496 07 au, respectively. The 3-21G energy for the related $C_4H_3^+$ fragment is 151.841 51 au and for $C_5H_3^+$ 189.496 07 au.

[31] Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1985**, *113*, 291.

Hypercoordinate Molecules of Second-Row Elements: d Functions or d Orbitals?

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Contribution from the Department of Chemistry, University College, ADFA, University of New South Wales, Campbell ACT 2601, Australia. *Received February 15, 1990*

Abstract: A new analysis of the d function contributions to the ab initio wave functions of hypercoordinate and normal valency compounds is reported for molecules of first- and second-row elements, all calculated at a comparable level. Energy minimization calculations show that the optimum d function exponent for any element changes very little from one compound to another, even those as different as H_2S and SF_6. There is no support for the view that diffuse d orbitals on the central atom take part in bonding after being contracted in the field of electronegative oxygen or fluorine atoms around the periphery. Although the level of participation of the supplementary functions in the wave functions of the hypercoordinate compounds is greater than in normal valency compounds, there is no difference in the role of the d functions. The effect of the added functions on calculated energy also provides no clear demarcation between the two classes; in S–F compounds, which are typical, the energy improvement per bond is much the same in SF_2 as it is in SF_6. The occupations of the higher order functions are quite strongly dependent on the degree of charge transfer from the central atom and on the number of electron pairs formally arranged around the central atom. d functions added to the basis sets of peripheral atoms like O or F produce just as large an energy improvement as that gained by putting d functions on the central second-row atom. It follows from the evidence that atom-centered molecular wave functions require functions higher in order than s and p functions to properly respond to the rapidly varying molecular potential in the space between the nuclei. Accordingly, any resemblance between d functions in molecular wave functions and the valence d orbitals of excited second-row atoms is an artifact of the electronic structure model; they should not be called "d orbitals".

It is generally agreed that electronic structure calculations on main group molecules would be seriously compromised without d functions in the basis sets of second-row atoms,[1-4] but there is wide disagreement about their role. Structure or reactivity studies