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Structures and Energies of $C_4H_2^{2+}$[1]

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Abstract: At the MP3/6-31G*//HF/6-31G* level of ab initio theory, the lowest energy $C_4H_2^{2+}$ dication is indicated to have a linear ($D_{\infty h}$) structure; the four-membered-ring (D_{2h}) alternative is 13.3 kcal/mol less stable. At MP4SDQ/6-31G*//3-21G the linear C_4H^+ ($C_{\infty h}$) monocation is only 3.6 kcal/mol more stable than its four-membered-ring (C_{2v}) isomer. These stability orders differ from those of the C_4 structures where the cyclic isomer (D_{2h}) is 0.7 kcal/mol (MP4SDQ/6-31G*//6-31G*) more stable than the linear ($D_{\infty h}$) structure. Despite the estimated very large heat of formation of $C_4H_2^{2+}$ of 733 kcal/mol, all the modes of dissociation explored are calculated to be endothermic. In particular, the surprisingly large proton affinity of C_4H^+, 63.1 kcal/mol, may be attributed to the diminution of electrostatic repulsion in the long, linear structure. In agreement with gas-phase studies, we find the most favorable $C_4H_2^{2+}$ dissociations to be into $C_3H^+ + CH^+$ (endothermic by 36.7 kcal/mol for **1**) and into $C_3H_2^+ + C^+$ (endothermic by 14.7 kcal/mol for **2**). All the four-membered-ring structures, $C_4H_2^{2+}$, C_4H^+, and C_4, show σ-deficient character for the bridging carbons. In these cases the HOMO's are σ orbitals of nonbonding nature with the significant stabilization resulting from 4-center, 2-electron aromatic π bonding. This result is contrary to intuition, which suggests double bond character between the bridging carbons as allowed for by an inverted geometry of the two sp^2-hybridized carbons.

Hydrocarbon dications with the general formulae $C_nH_2^{2+}$ and $C_nH_6^{2+}$ are particularly common in mass spectrometry.[2] These species usually have been represented by the linear structures $H{-}C_n{-}H^{2+}$ and $CH_3{-}C_{n-2}{-}CH_3^{2+}$, respectively,[2a] although no definite experimental evidence is available. Recent theoretical studies[3] on $C_6H_6^{2+}$ have suggested nonlinear structures to be energetically more favorable, and this even includes isomers which dissociate by loss of CH_3^+, an experimentally observed process.[4] Little is known about the structures of $C_nH_2^{2+}$ species experimentally. In a recent mass spectrometric paper on a number of dications, Rabrenovic and Beynon[5] presented evidence for the existence of two $C_4H_2^{2+}$ isomers. This is the subject of the present paper which continues our theoretical investigations of dications. Results on $C_2H_2^{2+}$ have been reported previously, and a comprehensive study of linear $H{-}C_n{-}H^{2+}$ dications will be presented subsequently.

Due to the isoelectronic relationship of $C_4H_2^{2+}$ with C_4H^+ and with C_4 (previously reported),[6] we will discuss their relationship in some detail. A comparison of the results with the neutral C_4H_2 isomers diacetylene and trialene[7] also is instructive.

These analogies suggest that the most favorable $C_4H_2^{2+}$ structures will be linear (**1**) and comprise a formally bicyclic four-membered-ring system (**2**). We confirm this expectation in the present study; branched and three-membered-ring structures are higher in energy. Qualitative molecular orbital considerations predict correctly that linear $C_4H_2^{2+}$ (**1**) will have a triplet ground state. Removal of one electron from each of the two orthogonal π systems of diacetylene allows each of the positive charges to be delocalized independently. This configuration plus the long, linear geometry reduces the Coulomb repulsion.

Although **2** is destabilized by the strained four-membered-ring system and by the enhanced Coulomb repulsion due to the relatively compact system, it is expected to benefit from the two-π-electron aromatic system. The electronic structure of **2** also provides another example of σ-deficient bonding between bridgehead carbons which recently has received much attention in the case of [1.1.1]propellane.[8]

Methods and Results

The calculational methods used in the GAUSSIAN 80 and 82 series of programs[8] are the Hartree–Fock (HF) theory followed by a Møller–Plesset (MP) perturbation evaluation[9] of electron correlation contributions. The triplet **1** is treated by spin-unrestricted (UHF) theory[10] and the corresponding unrestricted Møller–Plesset (UMP) expansion.[11] Standard basis sets were used.[12] Since the ground-state electronic configurations of **1** (triplet) and **2** (singlet) have different multiplicities, it is imperative to include the effect of electron correlation in the ab initio calculations in order to evaluate their relative ab initio energies.

The computations were carried out in two stages. In the preliminary investigation of $C_4H_2^{2+}$, optimized geometries for structures **1**–**9** were obtained at the HF/4-31G level, followed by single point calculations at MP2/4-31G and HF/6-31G*. The latter are denoted by MP2/4-31G//4-31G and HF/6-31G*//

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Table I. Total (in au) and Relative (in kcal/mol) Energies of $C_4H_2^{2+}$ Isomers[a]

structures		4-31G//4-31G	MP2/4-31G//4-31G	6-31G*//4-31G	est MP/6-31G*
1	D_{∞} triplet	-151.400 14 (0.0)	-151.672 19 (0.0)	-151.616 50 (0.0)	0.0
2	D_{2h}	-151.240 58 (100.1)	-151.615 49 (35.6)	-151.534 68 (51.3)	-13.2
3	D_{2h} triplet	-151.230 88 (106.2)	-151.560 02 (70.4)	-151.507 69 (68.3)	32.5
4	C_{2v}	-151.309 21 (57.1)	-151.589 23 (52.1)	-151.551 61 (40.7)	35.7
5	C_{2v}	-151.319 27 (50.7)	-151.609 09 (39.6)	-151.532 11 (53.0)	41.9
6	C_s triplet	-151.311 91 (55.4)	-151.590 37 (51.3)	-151.526 40 (56.5)	52.4
7	C_{2v}	-151.246 71 (96.3)	-151.499 08 (108.6)	-151.466 87 (93.9)	106.2
8	C_{2v}	-151.210 27 (119.1)	-151.470 88 (126.3)	-151.433 41 (114.9)	122.1
9	C_{2v} triplet	-151.286 59 (71.3)			

[a] Estimated relative energies, see Methods and Results

Table II. Total (in au) and Relative (in kcal/mol) Energies of $C_4H_2^{2+}$, C_4H^+, and C_4 Isomers[a]

structures		6-31G*//6-31G*	MP2/6-31G*//6-31G*	MP3/6-31G*//6-31G*
1	$D_{\infty h}$	-151.616 60 (0.0)	-152.006 02 (0.0)	-152.034 94 (0.0)
2	D_{2h}	-151.539 98 (48.1)	-152.008 38 (-1.5)	-152.013 72 (13.3)
10	$C_{\infty h}$	-151.514 71 (0.0)	-151.899 59 (0.0)	-151.931 48 (0.0)
11	C_{2v}	-151.456 93 (36.3)	-151.920 29 (-13.0)	-151.931 17 (0.2)
12	$D_{\infty h}$	-151.183 72 (0.0)	-151.590 51 (0.0)	-151.618 23 (0.0)
13	D_{2h}	-151.145 98 (23.7)	-151.613 70 (-14.6)	-151.622 53 (-2.7)
$C_3H_2^+$	$D_{\infty h}$	-114.313 24	-114.626 29	-114.644 51
C^+		-37.287 08	-37.331 07	-37.345 85

[a] HF/3-21G geometry.

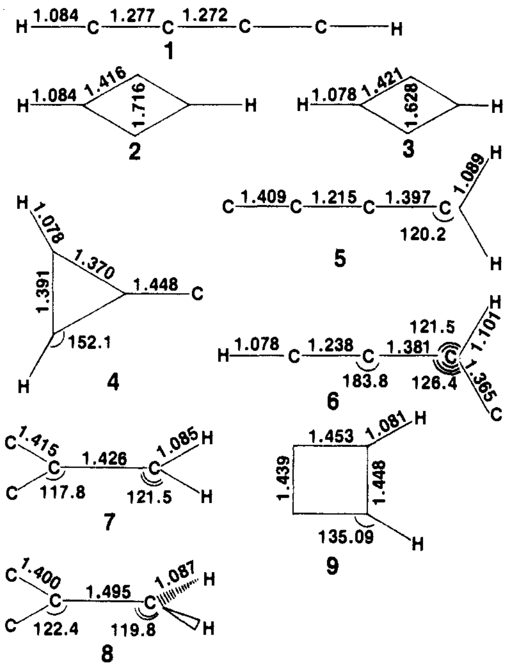

Figure 1. 4-31G optimized $C_4H_2^{2+}$ structures.

4-31G, the // symbol meaning "at the geometry of". The higher level MP2/6-31G*//4-31G data were then estimated by assuming that the correlation corrections were the same for both basis sets. These results, summarized in Figure 1 and Table I, indicate that branched $C_4H_2^{2+}$ structures and those containing three-membered rings are not competitive with **1** and **2**, so we have not characterized structures **3** to **9** as minima, saddle points, etc.

In the second state, the geometries of **1** (linear triplet) and **2** (singlet rhombus) were reoptimized at more advanced levels, together with the related molecules and fragments **10–13**. Hartree–Fock structures were obtained with the polarized 6-31G* basis. Subsequent single-point calculations were carried out including valence electron correlations by second- and third-order Møller–Plesset theory. The final level of theory is MP3/6-31G*//HF/6-31G*. The 6-31G* optimized geometries of **1**, **2**, and **11–13** are given in Figure 2, together with the 3-21G geometry of **10** (because of convergence problems, it was not possible to obtain the 6-31G* geometry of this species). The corresponding energies are listed in Table II.

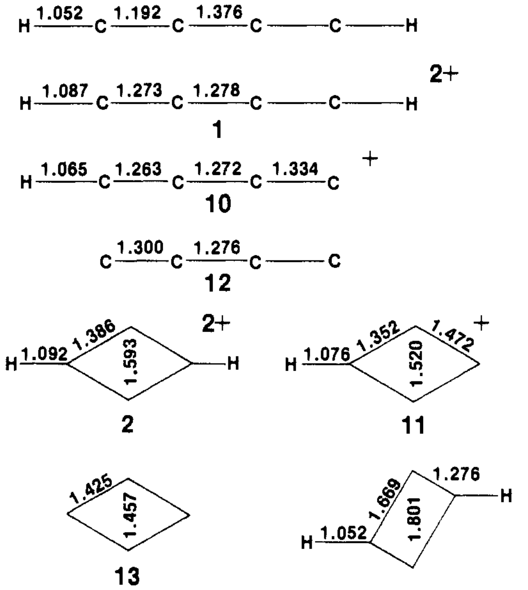

Figure 2. Optimized 6-31G* structural parameters for **1**, **2**, **10** (3-21G), **11**, **12**, **13**, diacetylene (4-31G), and trialene (4-31G).

Discussion

Geometries. The Linear Structures. Adiabatic dioxidation of diacetylene C_4H_2 results in the triplet diacetylene dication **1** ($D_{\infty h}$). That the C–C bonds are of nearly equal length, i.e., 1.278 (1.272) Å at 6-31G* (4-31G) for the central bond and 1.273 (1.277) Å for the terminal linkage, reflects the effective delocalization of the two charges in the orthogonal π planes. For comparison the C–C bond lengths in diacetylene are 1.192 and 1.376 Å (4-31G).[6]

The bond distances in dication **1** are comparable to those in the neutral linear C_4 molecule (**12**, $D_{\infty h}$), which has bond lengths of 1.276 and 1.300 Å at 6-31G*. Similar lengths are calculated for the linear C_4H^+ monocation **10** at the 3-21G level; however, we were unable to obtain its 6-31G* geometry, due to instability of the UHF wave function. Different electronic states for linear C_4H^+ are close in energy.

The Four-Membered-Ring Structures. The structure of cyclic **2** (D_{2h}) reveals interesting features. First, the short C–C bonds, 1.386 (1.416) Å at 6-31G* (4-31G), indicate significant double bond character. Second, the distance of 1.593 (1.716) Å between the "bare" (inverted) carbons is also short and suggests a bonding interaction. The geometrical dependence on the calculational level

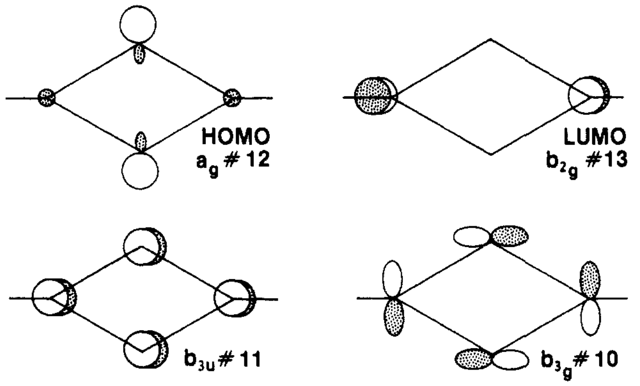

Figure 3. Selected MO's of **2**. In trialene (C_4H_2) the b_{2g} (MO no. 13) is the HOMO.

is common for highly strained species.[5,13] A more condensed ring system is obtained with the polarized 6-31G* basis, and the geometrical parameters should be more reliable.

In order to understand the electronic structure of **2** it is helpful to recall the characteristic bonding in the strained propellanes which also have inverted carbons.[7] The central bridgehead C–C bond (1.543 Å, 6-31G*) in [1.1.1]propellane is characterized as being "σ-deficient".[7,14] Its MO (the HOMO) is nearly nonbonding in character with the electron density located outside the "σ bond". The CH_2 bridges stabilize (3c-2e bonding) the short "nonexisting bond".

The cyclic structure **2** shows similar characteristics as [1.1.1]propellane. Both the "bare" carbons in **2** display an inverted geometry relative to an sp^2-hybridized carbon in typical olefins. As a result **2** also is σ bond deficient.[15] Indeed the HOMO indicates the nonbonding character with the electron density located outside the dication (see Figure 3). The stabilization results both from aromatic π bonding (orbital no. 11, b_{3g}) and from σ ring bonding (orbital no. 10, b_{3g}). The calculations thus suggest that the central bonding at most carries π character.

The C_4H^+ monocation ring structure (**11**, C_{2v}) shows behavior similar to **2**. The central 6-31G* C–C distance has shortened to 1.520 Å due to reduced electrostatic repulsion. One of the two ring C–C bonds is shorter, 1.352 Å, and one is longer, 1.472 Å, as compared to **2**. The smaller coefficient of the p_z orbital of the carbenoid center in the π bonding orbital is in part responsible for these calculated geometrical changes from **2**. The important feature of σ-deficient bonding, however, is also operative in this monocation: again the HOMO indicates nonbonding σ character between the central C atoms with the electron densities located outside the molecule.

It is illustrative to compare the reported neutral cyclic C_4 (**13**, D_{2h})[5] with **2**. The central 6-31G* C–C distance is expectedly shorter, i.e., 1.457 Å, with a slightly longer ring C–C bond, i.e., 1.425 Å, than in **2**. The MO frameworks are, however, quite similar. Their only difference is the symmetrical and antisymmetrical bonding combinations of the carbenoid centers vs. those of the C–H bonds in **2**. Also illustrative of the σ-deficient bonding between the central carbons of cyclic C_4, C_4H^+, and $C_4H_2^{2+}$ (**2**) are their (6-31G*) Mulliken overlap populations, although care must be exercised with this criterion. These values for C_4, C_4H^+, and $C_4H_2^{2+}$ (**2**) are negative, −0.0628, −0.0133, and −0.2356, respectively.

In simple Lewis terms, the bonding of the bridgehead C atoms in the cyclic C_4 (**13**), C_4H^+ (**11**), and $C_4H_2^{2+}$ (**2**) species may be described as follows: (a) two valence electrons each are involved in the ring C–C bonding, (b) the third electron participates in the aromatic ring π bonding, while (c) the fourth is σ nonbonding.

Relative Energies. At the split valence 4-31G basis level, **2** is 100 kcal/mol higher in energy than **1**. Inclusion of d functions lowers the relative energy of **2** drastically. This effect of polarization functions on highly strained hydrocarbons has been noted before.[5,13] The effect of electron correlation on lowering the relative energy of **2** is nearly as large.

Hartree–Fock theory is well-known not to give satisfactory energy differences between singlet and triplet isomers. As illustrated by the Møller–Plesset results, corrections for electron correlation give larger energy lowerings for singlet states. At the MP2/6-31G* level, the cyclic structure **2** actually becomes more stable than **1** by 1.5 kcal/mol. However, this level of theory tends to overestimate the correlation effect on the singlet–triplet difference. At the MP3 level, the linear structure **1** remains more stable by 13.3 kcal/mol. While higher expansion levels (e.g., MP4, which we could not investigate) may favor **2** relatively, it seems reasonable to conclude that **1** probably remains the most stable isomer. Geometries, optimized with inclusion of correlation corrections, could not be obtained due to computer time limitations.

Similar trends in the dependence of energy differences between **1** and **2** ($C_4H_2^{2+}$) with the theoretical levels were obtained for the linear and cyclic structures of C_4H^+ and of C_4. The data are compiled in Table II.

The most stable structure changes from linear to cyclic upon deprotonation of $C_4H_2^{2+}$. Thus the lowest energy $C_4H_2^{2+}$ dication is linear and is 13.3 kcal/mol (MP3/6-31G*//HF/6-31G*) more stable than the cyclic isomer. In the monocation, C_4H^+, this energy difference is reduced to only 0.2 kcal/mol (same level). In unprotonated C_4, the cyclic structure becomes more stable than the linear form by a modest −2.7 kcal/mol (same level).[16] For comparison, the four-π cyclic C_4H_2 isomer, "trialene" (C_{2h}, singlet), is 64.4 kcal/mol (est. MP2/6-31G*//HF/4-31G) less stable than linear diacetylene.[6] Hence, the relationship between the 4πe trialene and its 2πe dication is similar to that of cyclobutadiene (4πe) and its dication (2πe).[17]

Note the remarkably large (86.8 kcal/mol) reduction in the relative energies of **1** and **2** in going from the HF/4-31G//HF/4-31G to the MP3/6-31G*//HF/6-31G* level of theory. A similar reduction in relative energies for **12** and **13** of 83.3 kcal/mol (from HF/3-21G//HF/3-21G to MP3/6-31G*//HF/6-31G*) has been noted before.[5] These cases underline the importance of polarization functions and corrections for electron correlations in the theoretical levels for calculating small cyclic hydrocarbons.

Dissociations. Stepwise deprotonation of the linear dication **1** would give linear C_4H^+ (**10**) and subsequently linear C_4 (**12**) (eq 1 and 2). Both processes are endothermic, by 64.9 (MP3/6-31G*) and by 261.5 kcal/mol (MP3/6-31G*//HF/6-31G*), respectively.

$$\underset{\mathbf{1}}{C_4H_2^{2+}} \rightarrow \underset{\mathbf{10}}{C_4H^+} + H^+ \ (\Delta H^\circ = 64.9\ \text{kcal/mol}) \qquad (1)$$

$$\underset{\mathbf{1}}{C_4H_2^{2+}} \rightarrow \underset{\mathbf{12}}{C_4} + 2H^+ \ (\Delta H^\circ = 261.5\ \text{kcal/mol}) \qquad (2)$$

In particular, the large proton affinity of 64.9 kcal/mol for linear C_4H^+ is due to the diminution of electrostatic repulsion in the long carbon chain. Much of the charge resides on the hydrogens, which are as far apart as possible. For comparison the proton affinity of the related C_2H^+ is −9.8 kcal/mol (MP4SDTQ/6-31G**//HF/6-31G** + ZPE).[18]

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(16) At the MP4SDQ/6-31G*//HF/6-31G* level rhombic **13** is 0.7 kcal/mol more stable than linear **12**.[6] Dr. I. Shavitt finds linear C_4 to be slightly more stable than the rhombus, using multireference CI and Huzinaga-Dunnings's DZP basis sets; presented at the 188th ACS National meeting in Philidelphia, August, 1984, and at the 39th Symposium on Molecular Spectroscopy, Ohio State University, June 1984. Dr. J. P. Ritchie calculates the rhombic form to be 1.2 kcal/mol more stable than linear C_4; personal communication.

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(18) Pople, J. A.; Frisch, M. J.; Krishnan, R.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 468. Dr. A. Sawaryn, Erlangen (to be published), has calculated a high barrier to proton loss from **1** (111 kcal/mol at 3-21G//3-21G). Such barriers in linear $C_nH_2^{2+}$ dications increase regularly as the systems become larger and the charges are separated more effectively. See also ref 22.

The stepwise deprotonations of cyclic **2** to cyclic C_4H^+ and then to cyclic C_4 are also endothermic (eq 3 and 4) by 51.8 and 245.5 kcal/mol (MP3/6-31G*//HF/6-31G*), respectively. While **11** also has a large proton affinity, this is somewhat less favorable than that of **10**, since the hydrogens in **2** (which bear much of the positive charge) are not as far apart as those in **1**. The fragmentations of **1** and **2** into two C_2H^+ ($^3\Pi$) cations[19] also are endothermic by 72.0 (eq 5) and by 58.7 kcal/mol (MP3/6-31G*//HF/6-31G*), respectively. The dissociation of **1** and **2** into C_3H^+[19] and CH^+[19] is thermodynamically unfavorable by 36.7 (eq 6) and 23.4 kcal/mol, respectively (same level). The fragmentation of the four-membered-ring $C_4H_2^{2+}$ isomer **2** into $C_3H_2^+$ and C^+[20] is endothermic by a modest 14.7 kcal/mol (eq 7); for structural reasons, it seems unlikely that the similar dissociation of **1** (endothermic by 28.0 kcal/mol) would result in these fragments.

$$\underset{\mathbf{2}}{C_4H_2^{2+}} \rightarrow \underset{\mathbf{11}}{C_4H^+} + H^+ \ (\Delta H^\circ = 51.8 \text{ kcal/mol}) \quad (3)$$

$$\underset{\mathbf{2}}{C_4H_2^{2+}} \rightarrow \underset{\mathbf{13}}{C_4} + 2H^+ \ (\Delta H^\circ = 245.5 \text{ kcal/mol}) \quad (4)$$

$$\underset{\mathbf{1}}{C_4H_2^{2+}} \rightarrow C_3H^+ + CH^+ \ (\Delta H^\circ = 36.7 \text{ kcal/mol}) \quad (5)$$

$$\underset{\mathbf{1}}{C_4H_2^{2+}} \rightarrow 2C_2H^+ \ (\Delta H^\circ = 72.0 \text{ kcal/mol}) \quad (6)$$

$$\underset{\mathbf{2}}{C_4H_2^{2+}} \rightarrow C_3H_2^+ + C^+ \ (\Delta H^\circ = 14.7 \text{ kcal/mol}) \quad (7)$$

That all these modes of dissociation are calculated to be endothermic may not be surprising. For example, proton loss from the smaller acetylene dication, $C_2H_2^{2+}$, was calculated to be only slightly exothermic (9.8 kcal/mol) and to have a sizable barrier (65 kcal/mol).[18] Similarly, the ethylene dication was calculated to have a modest heat of deprotonation of 16.4 kcal/mol and a substantial barrier of 69 kcal/mol.[21] The stability of the $C_nH_2^{2+}$ dications increase further on elongation of the carbon chain. These species, like $C_4H_2^{2+}$ (probably two isomers), are particularly abundant in doubly charged ion mass spectrometry, and are generated both by electron ionization and by charge-stripping techniques. The fragmentation of $C_4H_2^{2+}$ in the gas phase may be due to its formation (in part) in electronically and/or vibrationally excited states.[22]

Our calculational data are in agreement with the experimental observation of Rabrenovic and Beynon;[5] there are two $C_4H_2^{2+}$ isomers, which lead to different fragments on dissociation. Our data showing that the lowest energy fragmentation of the linear isomer is into C_3H^+ and CH^+ also are consistent with experiment. The gas-phase study suggests that a second isomer dissociates into $C_3H_2^+$ and C^+.[5] The four-membered-ring structure **2** is the most likely candidate for this second isomer, although the C-substituted cyclopropenium ring structure **4** or the branched chain isomers **5** and **6** cannot be excluded since they are relatively low in energy.

The heat of formation of **1** can be evaluated from reactions 5 and 6 with use of the values (in kcal/mol) for the fragments CH^+ (exptl 387),[23] C_2H^+ (calcd 404,[19] exptl 399–414),[22] C_3H^+ (calcd 383,[19] exptl 383, 384, and 387),[24] and $C_3H_2^+$ (exptl 329)[25] and the calculated heats of reactions (eq 5 and 6). The lower heat of formation of **1** is 726 kcal/mol. Although this large value suggests significant thermodynamic instability, the explored dissociation modes are indicative for at least significant kinetic stability for $C_4H_2^{2+}$. This would explain its frequent mass spectroscopic observation.

Conclusions

The global $C_4H_2^{2+}$ energy minimum is calculated to be the triplet linear diacetylene dication **1**. The cyclic singlet **2** is 13.3 kcal/mol higher in energy. The lowest estimated heat of formation of **1** is 726 kcal/mol. Both **1** and **2** are thermodynamically stable toward the likely modes of dissociation by at least 1 eV; a rather high barrier further impeeds proton loss and this is to be expected for the other dissociation processes as well. The existence of both linear and cyclic isomers close in energy and leading to different fragments ($C_3H^+ + CH^+$ and $C_3H_2^+ + C^+$) by endothermic dissociation is consistent with experimental observations. The isoelectronic relationship for both **1** and **2** between the structurally similar $C_4H_2^{2+}$, C_4H^+, and C_4 species is revealing. All these cyclic structures, with inverted geometries for the bridging carbons, display σ-deficient bonding. These structures have a nonbonding σ orbital as HOMO and are stabilized significantly by 4c–2e π bonding.

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