is therefore a complete one-to-one correspondence between the MO approach's essential results and the consequences of the effective valence bond model.[30]

The whole discussion has been derived by using a semiempirical effective valence bond Hamiltonian in that sense that it was derived from the Pariser–Parr–Pople N-electron Hamiltonian. A forthcoming paper[17] will show that the effective valence bond Hamiltonian may be derived from ab initio calculations as well (even in nonminimal basis sets), and this nonempirical EVB Hamiltonian will allow one to calculate directly the energy and conformations of conjugated molecules in the ground and excited neutral states without using any empirical relationship. The numerical predictive performances will be much better, but the whole analysis (given in the present paper) of the electronic assembly as being governed by spin ordering will be kept.

Appendix

The calculation of the statistical indices may be illustrated for the case of the lowest states of the butadiene molecule, for which, including small three body operators, the following holds:

	S^t	T^t
$1\bar{2}3\bar{4}$	0.556	0.651
$\bar{1}2\bar{3}4$	0.556	−0.651
$1\bar{2}\bar{3}4$	−0.412	0
$\bar{1}23\bar{4}$	−0.412	0
$\bar{1}\bar{2}34$	−0.144	0.276
$12\bar{3}\bar{4}$	−0.144	−0.276

The probability of finding a β spin on j when i bears on α spin $\mathcal{P}_{ij}{}^{A}$ is given by

$$\mathcal{P}_{12}{}^{A,S^t} = [(0.556)^2 + (0.412)^2]/0.5 = 0.959$$

$$\mathcal{P}_{14}{}^{A,T^t} = [(0.651)^2 + (0.276)^2]/0.5 = 1.0$$

The probability of finding a singlet distribution between i and j may be calculated as follows:

$$\mathcal{P}_{23}{}^{S,S^t} = [\tfrac{1}{2}(0.556 + 0.144)^2] = 0.490$$

$$\mathcal{P}_{14}{}^{S,T^t} = [\tfrac{1}{2}(0.651 - 0.276)^2] = 0.140$$

One may see, for instance, that the strong spin alternation between atoms 1 and 4 in the lowest triplet state essentially corresponds to a triplet arrangement.

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(30) One frequently uses the terms of effective Hamiltonians for ad hoc operators which are required to mimic the behavior of the "exact" one in a certain range of energies and for some functional subspace.[31] One may, for instance, use least-square fittings to determine such classes of pseudo-Hamiltonians, as has been done by Durand et al. for the determination of core pseudopotentials[32] or monoelectronic pseudo-Hartree–Fock Hückel-type operators.[31] The analytic form of these pseudooperators remains quite arbitrary, and we think that *these pseudooperators should be distinguished from the effective operators* which are *deduced* from the "exact" ones by first principle operators such as the QDPT[1,6] (see, for instance, the work of Freed et al.[33]) or the wave operator formalism.[8] The deduced effective operators handle a projected information and are perfectly rigourous; they may be perfectly exact (if the perturbation expansion converges), giving exact energies and components of the exact wave functions in the model space. They may be thought of as exact projected Hamiltonians leading to exact (projected) alternative descriptions of the molecular electronic order; the above discussed spin ordering description is such an alternative exact effective (or projected) description, which is of course nonunique since it depends on the choice of the model space, which is unable to give valuable information on the states having small components on this model space, but which may represent a powerful instrument.

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The Ethylene Dication: A Theoretical Study of the $C_2H_4{}^{2+}$ Potential Energy Surface[1]

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Abstract: The $C_2H_4{}^{2+}$ potential energy surface was examined by ab initio molecular orbital theory corrected for electron correlation by means of Møller–Plesset perturbation theory to third order (MP3/6-31G**) using 6-31G* (and 3-21G) optimized geometries. The perpendicular (D_{2d}) ethylene dication, **1** (D_{2d}), is the global and only singlet $C_2H_4{}^{2+}$ minimum with an estimated heat of formation of 654 kcal/mol. The rotational transition structure, **2** (D_{2h}), is 28.1 kcal/mol higher in energy. This rotational barrier is remarkably large for such 14-electron species (compare H_2BBH_2 and $H_2B\text{–}CH_2{}^+$, 10.5 and 20.1 kcal/mol, respectively). The C_{3v} ethylidene dication, **4**, 21.3 kcal/mol higher in energy than **1**, is probably not a minimum, but may facilitate hydrogen scrambling. Although **1** is unstable thermodynamically toward proton loss (by 16 kcal/mol), the barriers for deprotonation (and homolytic cleavage (into two $CH_2{}^+$ cations)) are 68.8 and about 88.4 kcal/mol, respectively. The transition structure for cleavage of **4** into $CH_3{}^+$ and CH^+ lies 86.5 kcal/mol above **1** in energy. These large barriers are consistent with the experimental observation of $C_2H_4{}^{2+}$ in the gas phase.

Many important reactions of ethylene, the largest volume organic chemical produced today, involve oxidative processes.[3] The most basic oxidations of ethylene are the one-electron process leading to the radical cation, $C_2H_4{}^{+\cdot}$, and the two-electron loss leading to the dication, $C_2H_4{}^{2+}$. The ethylene radical cation is a commonly observed species in the gas phase and is produced,

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[1] Considered as Carbodications Part 6 by the group in Erlangen. For Part 5, see ref 16g.

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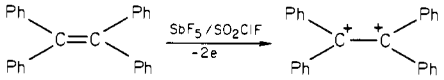
e.g., mass spectroscopically and by photoionization spectroscopy.[4] The ionization potential of ethylene is 10.51 eV.[4] The formation and reactions of $C_2H_4^{+\cdot}$ in the gas phase have been well studied.[5] For example, the ethylene radical cation reacts with ethylene to form $C_4H_8^{+\cdot}$ intermediates.[5c] In solution, dimerizations of methyl- and phenyl-substituted ethylene radical cations have been considered, but never proven, as the initiation step of cationic polymerization of certain electron-rich olefins.[6]

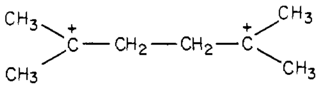
In contrast, the double ionization of ethylene, while known in the gas phase,[7] has not been well investigated. A double-ionization potential was measured by double mass charge transfer spectroscopy. In connection with this experimental spectrum, theoretical ab initio calculations were reported, but only for the vertical transitions involving the planar $C_2H_4^{2+}$ configuration.[7a]

In solution, the direct two-electron oxidation of ethylene substituted by aryl groups was realized in our preceding experimental work.[8]



An X-ray structure of the tetra-*tert*-anisylethylene dication reveals a 41° twist around the central C–C bond.[9] So far no direct observation of the dioxidation of the parent ethylene has been achieved in the condensed phase, and we wondered if the ethylene dication might be a viable intermediate, e.g., in the claimed ionic group polymerization of ethylene and methane with SbF_5-containing super acids.[10]

Carbodications are an emerging class of remarkable molecules. Many examples are known in solution.[11] The simplest aliphatic carbodication which has been observed directly in solution has the two trigonal formally charged centers in a 1,4 relationship. Closer proximity does not appear to be possible in the absence of special stabilization. In the gas phase,



$$(CH_3)_2\overset{+}{C}-CH_2-CH_2-\overset{+}{C}(CH_3)_2$$

charge stripping mass spectrometry and other methods of generating dications have led recently to the observation of a great number of hydrocarbon dications, even very small molecules where coulombic repulsion is expected to be very large.[12] The structures

Chart I

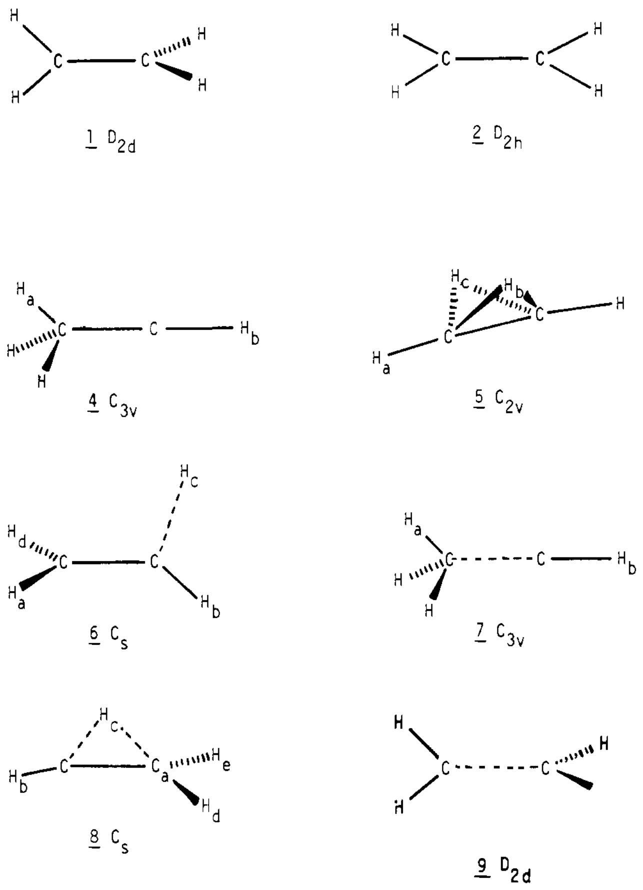


Table I. HF/6-31G* and HF/3-21G Geometries of $C_2H_4^{2+}$ Structures[a]

structure	geometry
1 (D_{2d})	C–C = 1.432 (1.409); C–H = 1.103 (1.106); ∠HCC = 120.1 (120.8)
2 (D_{2h})	C–C = 1.587 (1.617); C–H = 1.090 (1.090); ∠HCC = 119.2 (118.9)
4 (C_{3v})	C–C = 1.309 (1.300); C–H$_a$ = 1.141 (1.151); C–H$_b$ = 1.112 (1.107); ∠HCC = 109.9 (112.9)
5 (C_{2v})	C–C = (1.244); C–H$_a$ = (1.099); C–H$_b$ = (1.396); ∠H$_a$CC = (172.0); ∠CH$_b$C = (52.9), ∠H$_b$CH$_c$ = (88.6)
6 (C_s)	C–C = 1.293 (1.285), C–H$_a$ = 1.093 (1.095); C–H$_b$ = 1.083 (1.080); C–H$_c$ = 2.791 (2.773); ∠H$_a$CC = 120.3 (121.2); ∠H$_a$CH$_d$ = 119.4 (117.5); ∠H$_b$CC = 155.8 (157.1); ∠H$_c$CC = 102.3 (103.5)
7 (C_{3v})	C–C = 1.950 (1.914); C–H$_a$ = 1.088 (1.092); C–H$_b$ = 1.120 (1.123); ∠HCC = 97.4 (98.7)
8 (C_s)	C–C$_a$ = (1.291); C–H$_b$ = (1.104); C$_a$–H$_c$ = (1.323); C$_a$–H$_d$ = (1.124); ∠H$_b$CC = (179.1); ∠H$_c$C$_a$C = (72.8); ∠H$_d$C$_a$C = (121.0); ∠H$_d$CH$_e$ = (115.6)
9 (D_{2d})	C–C = (2.450); CH = (1.089); ∠HCC = 111.7

[a] Bond lengths are in angstroms and bond angles in degrees. The 3-21G geometrical parameters are in parentheses. For the ethylene structure see ref 25: the 6-31G* geometry, C–C = 1.31 Å, C–H = 1.076 Å, and ∠HCC = 121.8°.

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Table II. Total (in au) and Relative (in kcal/mol) Energies of $C_2H_4^{2+}$ Structures, Ethylene, and Beryllium Ylide[a]

structures	negative eigenvalues (3-21G)	3-21G//3-21G	6-31G*//6-31G*	6-31G**//6-31G*
1, D_{2d}	0	−76.64454 (0)	−77.08671 (0)	−77.09538 (0)
2, D_{2h}[b]	1	−76.59987 (28.0)	−77.04742 (24.6)	−77.05536 (25.1)
3, D_{2h}	1	−76.54229 (64.2)	−76.99000 (60.7)	−76.99814 (61.0)
4, C_{3v}	0	−76.58309 (38.6)	−77.01745 (43.5)	−77.02701 (42.9)
5, C_{2v}	2	−76.53189 (70.7)		
6, C_s	1	−76.51698 (80.0)	−76.94812 (87.0)	−76.95482 (88.2)
7, C_{3v}	1	−76.52110 (77.5)	−76.95208 (84.5)	−76.96021 (84.8)
8, C_s	1	−76.57112 (46.1)	−77.02015 (41.8)[c]	−77.03221 (39.6)[d]
9, D_{2d}	1	−76.54558 (62.1)	−76.97897 (67.6)[c]	−76.98767 (67.6)[d]
ethylene, D_{2h}	0	−77.60099	−78.03172	−78.03884
H_2BeCH_2	1	−54.38114		

[a] 1 hartree = 627.49 kcal/mol. [b] The geometry of neutral ethylene is used at the various levels of calculations. [c] 6-31G*//3-21G. [d] 6-31G**//3-21G.

of such species are best investigated theoretically, and our groups have already reported calculational results for many examples.[1] We now extend our common interests to $C_2H_4^{2+}$.

With the exception of the limited investigation on the planar geometry mentioned above,[7a] no prior theoretical calculations on $C_2H_4^{2+}$ have been reported. However, it has long been recognized from qualitative molecular orbital arguments[13] that $C_2H_4^{2+}$, like other 14-electron A_2H_4 molecules (e.g., H_2BBH_2[14] and $H_2BCH_2^+$[15]), should prefer perpendicular (D_{2d}) rather than ethylene-like planar geometries. We now report a thorough study of the $C_2H_4^{2+}$ potential energy surface at sophisticated ab initio levels. We have explored bonding characteristics, ionization potentials, kinetic and thermodynamic stabilities, and fragmentation and isomerization processes with their activation barriers.

We hope the present investigation will further serve to encourage carbodication investigations. These may have been inhibited by the general expectation that such species would fragment spontaneously. While most small carbodications are thermodynamically unstable toward fragmentation, dissociation into two monocations is generally found to involve considerable activation barriers.[16] This explains the experimental observation of $C_2H_4^{2+}$ and similar dications in the gas phase.

Methods

The ab initio molecular orbital calculations have been carried out at the restricted Hartree–Fock level with a modified version of the GAUSSIAN 80 series of programs.[17] The minimal STO-3G basis[18a] was used for initial geometry optimizations and was found to be particularly useful for saddle-point searches. Structures **1–8**, chosen to characterize the $C_2H_4^{2+}$ potential energy surface, were then completely optimized within the assumed symmetries utilizing the split-valence 3-21G basis.[18b] Data are given in Table I which include geometries of **1–7** optimized with the polarization 6-31G* basis.[18c] The 6-31G* geometry optimization of **8** was unsuccessful (see below). Single-point calculations at the 6-31G** level[18c] (with additional p functions on hydrogen) were carried out on the 6-31G* optimized structures. Absolute and relative Hartree–Fock energies of **1–8** are listed in Table II. Valence electron correlation corrections were obtained with second- and third-order Møller-Plesset perturbation theory[19] with the 6-31G** basis set. A typical notation is MP3/6-31G**//6-31G*. These data are given in Table III.

Table III. 6-31G** Total (in hartrees) and Relative (in kcal/mol) Energies Based on 6-31G* Geometries

structures	MP2	MP3
1	−77.29809 (0)	−77.32626 (0)
2	−77.25015 (30.1)	−77.28080 (28.5)
3	−77.19078 (67.3)	−77.22076 (66.2)
4	−77.26989 (17.7)	−77.28830 (23.8)
6	−77.18680 (69.8)	−77.20750 (74.5)
7	−77.15612 (89.1)	−77.18844 (86.5)
8[a]	−77.27086 (17.1)	−77.29183 (21.6)
9[a]	−77.15423 (90.3)	−77.18532 (88.4)
ethylene	−78.31682	−78.33998

[a] The 3-21G optimized geometry is used.

Vibrational frequencies and zero-point vibrational energies (ZPE) of all the chosen structures, **1–8**, were derived (3–21G basis set) from the harmonic force constants by numerical differentiation of the analytically calculated energy gradient using internal coordinates. For transition structures the imaginary frequency is neglected in the zero-point summation. The number of negative eigenvalues (or imaginary frequencies) in the force constant matrix for the 3-21G optimized geometries was found to be zero (minima or equilibrium structures) for **1** and **4** and one (saddle points or transition structures) for **2**, **3**, **6**, **7**, and **8**; two negative values were found for **5**. While **4** was indicated to be a local minimum at 3-21G, this is not the case at higher theoretical levels (see below). The complete set of calculated harmonic frequencies and zero-point vibrational energies is listed in Table IV.

Results and Discussion

Ethylene Dication. The perpendicular (D_{2d}) ethylene dication (**1**) is the lowest energy $C_2H_4^{2+}$ structure (the global minimum). Adiabatic two-electron oxidation of planar ethylene (D_{2h}) thus

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Table IV. 3-21G Harmonic Frequencies[a] (cm^{-1}) and Zero-Point Energies (kcal/mol)

geometry	frequencies	ZPE
1, D_{2d}	797 (e), 872 (b_1), 1118 (a_1), 1320 (e), 1436 (b_2), 1451 (a_1), 2934 (b_2), 2958 (a_1), 3045 (e)	30.1
2, D_{2h}	877 (a_g), 901 (b_{3u}), 1109 (b_{2u}), 1234 (b_{2g}), 1388 (b_{3g}), 1490 (b_{1u}), 1545 (a_g), 3115 (b_{1u}), 3133 (a_g), 3268 (b_{2g}), 3271 (b_{3u}), 752* (a_u)	30.5
3, D_{2h}	1089 (b_{3u}), 1093 (b_{2u}), 1492 (b_{2g}), 1496 (b_{3g}), 1585 (a_g), 1691 (b_{1u}), 2046 (a_g), 3271 (b_{1u}), 3300 (a_g), 3374 (b_{2g}), 3376 (b_{3u}), 1873* (a_u)	34.0
4, C_{3v}	601 (e), 1017 (e), 1229 (e), 1326 (a_1), 1585 (a_1), 2543 (e), 2607 (a_1), 2992 (a_1)	27.6
C_{3v}[b]	290 (e), 993 (e), 1184 (e), 1201 (a_1), 1567 (a_1), 2671 (e), 2700 (a_1), 3082 (a_1)	26.9
5, C_{2v}	888 (a_1), 948 (b_1), 978 (b_1), 1085 (a_2), 1270 (a_1), 1649 (b_2), 1675 (a_1), 1938 (a_1), 3023 (b_1), 3186 (a_1), 1138* (a_2), 940* (b_2)	23.8
6, C_s	213 (a'), 491 (a''), 666 (a''), 773 (a'), 1149 (a'), 1194 (a''), 1388 (a'), 1678 (a'), 3066 (a'), 3147 (a''), 3283 (a'), 727* (a')	24.4
7, C_{3v}	664 (e), 1152 (e), 1446 (e), 1458 (a_1), 2825 (a_1), 3042 (a_1), 3230 (e), 552* (a_1)	29.0
8, C_s	642 (a''), 945 (a'), 1152 (a''), 1204 (a''), 1253 (a'), 1311 (a'), 1637 (a'), 1720 (a'), 2791 (a'), 2833 (a''), 3066 (a'), 893* (a')	26.5
9, D_{2d}	129 (b_1), 716 (e), 1084 (b_2), 1174 (e), 1270 (a_1), 3070 (b_2), 3088 (a_1), 3313 (e), 256* (a_1)	27.2

[a] The asterisk indicates the imaginary reaction coordinate frequency. [b] 6-31G* harmonic frequencies and zero-point energies.

results in a major change in geometry. The required energy is underestimated at Hartree–Fock levels (e.g. 25.67 eV at 6-31G**//6-31G*) since a change in the number of electrons is involved. Electron-correlation corrections increase this value, and provide our final estimate of 27.58 eV (MP3). No significant change is found at the higher MP4SDQ/6-31G**//6-31G level.

In contrast, the vertical double ionization of ethylene (Franck–Condon transition) results in a dication (**3**) with a geometry identical with that of ethylene. When this process is simulated calculationally, the closed shell singlet state is found to lie below the lowest triplet; the corresponding double-ionization potential is 30.45 eV (MP3/6-31G**//6-31G*). Experimentally, the reported double-ionization potential is 29.4 ± 0.05 eV.[7a] In the same study, the various electronic states of $C_2H_4^{2+}$ could be reproduced by SCF-CI calculations.[20] We emphasize that **3**, with the ethylene geometry, is an arbitrary point on the $C_2H_4^{2+}$ potential energy surface. Even the planar D_{2h} geometry optimized structure, **2**, is a saddle point. However, **2** is 37.7 kcal/mol more stable than **3** (MP3/6-31G**//6-31G*).

The calculated C–C bond length of ethylene (1.317 Å, 6-31G*) increases to 1.432 Å in **1**, but the latter is surprisingly short and actually compares to those of aromatic compounds. This indicates the source of the stability of **1** relative to the other forms of $C_2H_4^{2+}$. In **1**, the two formally vacant orbitals are othogonal and each interact hyperconjugatively with the corresponding vicinal CH_2 groups. The best charge distribution results. Positive charges reside primarily on the more electropositive hydrogen atoms; in the D_{2d} conformation these are as far apart as possible.

Full-geometry optimization of the dication within D_{2h} symmetry constraints results in structure **2**, 28.1 kcal/mol less stable than **1** (MP3/6-31G**//6-31G* with inclusion of the zero-point energy correction). Inspection of the normal mode of the reaction coordinate frequency establishes **2** to be the rotational transition structure. Thus, when the symmetry constraints are relaxed, optimization of **2** will result in the minimum, **1**.

The bond rotation not only affects the energy but also the geometry of the ethylene dication. Thus, the C–C bond length increases from 1.432 Å in **1** to 1.587 Å in **2**. This 0.155-Å lengthening is caused by the absence of hyperconjugation in **2**, and the greater electrostatic repulsion between in-plane vicinal hydrogens.

As we have noted before, the removal of two electrons generally results in a preference for anti-van't Hoff geometries.[21] Thus, CH_4^{2+} is planar rather than tetrahedral, and the molecule of present concern, $C_2H_4^{2+}$, is perpendicular (**1**) rather than planar. Ethylene strongly prefers the planar geometry; the experimental rotational barrier is 65 kcal/mol.[22] Even though the two π electrons are removed and the classical structure of **1** can be written with single bonds, the preference for the anti-van't Hoff perpendicular geometry, 28.1 kcal/mol, is remarkably large. Other electron-deficient species, e.g., the $C_4H_4^{2+}$, $C_5H_4^{2+}$, and $C_6H_4^{2+}$ cumulene dications[1e,f] and "BBC ring" systems,[21] also prefer anti-van't Hoff geometries. However, the rotational barriers generally are lower and the geometrical changes smaller.

Ethylidene Dication. A basically different $C_2H_4^{2+}$ structure, $H_3C–C–H^{2+}$ (**4**), is found to be a local minimum with the 3-21G and 6-31G* basis sets and can be defined by imposing C_{3v} symmetry. At higher theoretical levels, however, with inclusion of electron correlation this structure is likely not to be an energy minimum.

At 3-21G//3-21G a transition structure, **8**, for the **4** → **1** 1,2-hydride shift could be located and lies 7.5 kcal/mol above **4** in energy. However, both larger basis sets and electron-correlation corrections are known to favor such bridged structures preferentially and to reduce 1,2-H shift barriers considerably. The rearrangement of ethylidene to ethylene, $CH_3CH \rightarrow H_2C{=}CH_2$, is a case in point.[23] At 4-31G (comparable to 3-21G), a barrier of 19.9 kcal/mol is found; this is reduced to 14.1 and 11.4 at 6-31G* and 6-31G**, respectively. Electron correlation is indicated to remove the barrier completely. With **8**, this already appears to be the case with the 6-31G* basis set. A single-point calculation on **8** with use of the 3-21G-determined geometry gave an energy 1.7 kcal/mol below that of **4**, and similar results were found at higher levels. Attempted geometry optimizations of **8** at 6-31G* led only to **4** or **1**. We conclude that **8** is not a transition structure. Similar results have been reported for the isoelectronic species, $H_2C^+–BH_2$, which rearranges in the reverse direction to $H_3C–B^+H$ without activation.[15b] In the $C_2H_4^+$ series, the CH_3CH^+ (C_1) → $H_2CCH_2^+$ (D_{2h}) rearrangement also is indicated to have a small barrier at 6-31G**//6-31G* (1.7 kcal/mol), but this disappears at correlated levels.[24] In general, such 1,2-hydride shifts involving centers with formally vacant p orbitals involve low barriers, or none at all.

The energy difference between the ethylidene (**4**) and ethylene (**1**) dications also depends on the theoretical level employed. While the Hartree–Fock values (Table II) are more or less constant (e.g., 42.9 kcal/mol at 6-31G**//6-31*), much lower values are found when electron-correlation corrections are included. Our final estimate, 21.3 kcal/mol, combines the MP3/6-31G**//6-31G*

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(20) We note that the ab initio calculation of Benoit and Horsley[7a] give an absolute energy for $C_2H_4^{2+}$ (vertical excitation) of −76.9708 au and for the SCF-CI calculation of −77.0865 au. Our HF/6-31G* energy is lower and the subsequent electron correlation correction through MP2 and MP3 lower this energy and that of 6-31G** even significantly more. In other words our calculated energies are of higher accuracy. The obtained deviation from the experimental excitation energy could imply a larger experimental error than quoted.[7a]

(21) (a) Krogh-Jespersen, K.; Cremer, D.; Poppinger, D.; Pople, J. A.; Schleyer, P. v. R.; Chandrasekhar, J. *J. Am. Chem. Soc.* **1979**, *101*, 4843. (b) See ref 1e and 1f.

(22) Douglas, J. E.; Rabinovich, B. S.; Looney, F. S. *J. Chem. Phys.*, **1955**, *23*, 515.

(23) Raghavachari, K.; Frisch, M. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *85*, 145.

(24) Whiteside, R. A.; Frisch, M. J.; Binkley, J. A.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive"; 2nd ed., 1981 and more recent entries and unpublished results at higher levels.

value (23.8 kcal/mol) and the zero-point energy correction. Thus, $C_2H_4^{2+}$ dications should undergo rather rapid hydrogen scrambling at room temperature.

Even though CH_3–C–H^{2+} (**4**) is likely not to be an energy minimum, the degree of stabilization afforded by the methyl group is of interest. This is evaluated, relative to the parent H–C–H^{2+} dication,[1b] by means of eq 1. The magnitude far exceeds the

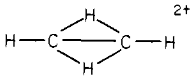
$$CH_2^{2+} + CH_3CH_3 \rightarrow \underset{\mathbf{4}}{CH_3CH^{2+}} + CH_4 \qquad (1)$$

$$-132.2 \text{ kcal/mol}$$

$$\text{MP3/6-31G**//6-31G*}$$

stabilizing effect of the methyl group in the ethyl cation (about 43 kcal/mol, using experimental values).[4a] The two orthogonal formally vacant p orbitals in **4** both interact hyperconjugatively with the methyl group. This distributes the charge to the more electropositive hydrogens, lengthens the C–H bonds, and shortens the C–C bond. In fact, the C–C distance in **4** (1.309 Å) is even less than the C═C double-bond length in ethylene (1.317 Å) and is much less than the value in **1** (1.432 Å).

Bridged Ethylene Dications. Since hydrogen bridging is a common feature in carbocations,[25] we also investigated singly and doubly hydrogen bridged forms of the ethylene dication. The most highly symmetrical possibility is a planar doubly bridged structure with D_{2h} symmetry.



However, preliminary investigations showed the energy of this form to be very unfavorable (98.4 kcal/mol less stable than **1** at STO-3G//STO-3G and 108.3 kcal/mol at 4-31G//4-31G) so that this possibility was not pursued further. It should be better, in effect, to protonate acetylene twice on each of the orthogonal π systems. This results in a structure (**5**) with C_{2v} symmetry. Optimization within this symmetry constraint led to a geometry with a nearly ideal (88.6°) angle between the bridging hydrogen planes. At both 3-21G//3-21G// and at 4-31G//4-31G, **5** is 70.6 kcal/mol above **1** in energy. In addition, **5** has two imaginary frequencies (Table IV) and is not a transition structure on the potential energy surface. Hence, **5** was not investigated further. We note that there is a geometrical relationship between **5** and what is most probably the most stable form of $C_2H_2Li_2$.[26]

At the 3-21G level (but only at this level), a singly bridged transition structure, **8**, was located. This can be viewed either as a π-protonated classical vinyl cation or as a corner-protonated bridged vinyl cation. As discussed above, higher theoretical levels stabilize such bridged structures preferentially, and **8** no longer corresponds to a definable point on the potential energy surface.

Thermodynamic Stabilities. Experimental heats of reaction for carbocations are reproduced reasonably well by ab initio theory. Notable examples in the present context are the hydrogenation of the methyl and ethyl cations and the stabilization energies, relative to CH_3^+, of higher carbocations.[25b]

Considering only the most likely processes, the $C_2H_4^{2+}$ ions might fragment in the following ways: **1** could lose a proton to give the bridged vinyl cation[25b] (eq 2) or cleave into two methylene cations (eq 3); methyl and methine cations might result from **4** (eq 4). The calculated energies for these processes are given below at the MP3/6-31G**//6-31G* level.[27]

$$\underset{\mathbf{1}}{H_2CCH_2^{2+}} \rightarrow C_2H_3^+ + H^+ \qquad -16.4 \text{ kcal/mol} \qquad (2)$$

$$\underset{\mathbf{1}}{H_2CCH_2^{2+}} \rightarrow 2CH_2^+ \qquad -1.7 \text{ kcal/mol} \qquad (3)$$

$$\underset{\mathbf{4}}{H_3CCH^{2+}} \rightarrow CH_3^+ + CH^+ \qquad -40.0\text{kcal/mol} \qquad (4)$$

The energy of eq 2, which becomes −23 kcal/mol when corrected for zero-point energy differences, can be combined with the experimental values, $\Delta H_f{}^\circ{}_0(C_2H_3^+)$ = 266 kcal/mol[4a,28] and $\Delta H_f{}^\circ{}_0(H^+)$ = 365.2 kcal/mol,[4a] to estimate $\Delta H_f{}^\circ{}_0(C_2H_4^{2+})$ = 654 kcal/mol. Using our calculated adiabatic ethylene double-ionization potential, 27.38 eV or 642 kal/mol, a zero-point correction of −4 kcal/mol associated with this process, and $\Delta H_f{}^\circ{}_0(C_2H_4)^{2+}$ = 14.5 kcal/mol,[4a] we obtain essentially the same value, $\Delta H_f{}^\circ{}_0(C_2H_4^{2+})$ = 652.5 kcal/mol.

Evaluation of the thermodynamics of the homolytic cleavage of **1** into two CH_2^+ radical cations (eq 3) is associated with multiplicity differences and is sensitive to correlation corrections. Although this process is exothermic by 28.7 kcal/mol at the HF/6-31G* level, this is reduced to 1.7 kcal/mol at MP3/6-31G**//6-31G*. Higher levels of theory may change this value further. Zero-point energy differences (ZPE's are 11.2[1a] and 30.1 kcal/mol for CH_2^+ and **1**, respectively) correct eq 3 to −9.4 kcal/mol. The experimental $\Delta H_f{}^\circ{}_0(CH_2^+)$ of 333.1 kcal/mol[29] gives $\Delta H_f{}^\circ{}_0(C_2H_4^{2+})$ = 657 kcal/mol, in quite reasonable agreement with the values above.

However, evaluation of eq 4 (zero-point correction 1.7 kcal/mol, experimental $\Delta H_f{}^\circ{}_0(CH_3^+)$ = 262 and -(CH^+) = 387 kcal/mol)[4a] leads to $\Delta H_f{}^\circ{}_0$(**4**) = 691 kcal/mol. Subtracting the 21.3 kcal/mol energy difference (MP3, ZPE corrected) between **4** and **1**, we obtain $\Delta H_f{}^\circ{}_0(C_2H_4^{2+})$ = 670 kcal/mol, significantly higher than the other values. We choose $\Delta H_f{}^\circ{}_0(C_2H_4^{2+})$ = 654 kcal/mol as the best estimate.

The extreme thermodynamic instability of the $C_2H_4^{2+}$ dication is emphasized by the disproportionation reactions, eq 5–7. These are evaluated by using the estimated $\Delta H_f{}^\circ(C_2H_4^{2+})$ = 654 kcal/mol and experimental heats of formation (at 0 K) of the other species.[4a] Hydride abstraction from methane (eq 5) and from ethane (eq 6) as well as electron transfer from ethylene to give two $C_2H_4^+$ radical cations (eq 7) are highly exothermic.

$$\underset{\mathbf{1}}{H_2CCH_2^{2+}} + CH_4 \rightarrow C_2H_5^+ + CH_3^+ \qquad -199.5 \text{ kcal/mol} \qquad (5)$$

$$\underset{\mathbf{1}}{H_2CCH_2^{2+}} + C_2H_6 \rightarrow 2C_2H_5^+ \qquad -156.3 \text{ kcal/mol} \qquad (6)$$

$$\underset{\mathbf{1}}{H_2CCH_2^{2+}} + C_2H_4 \rightarrow 2C_2H_4^+ \qquad -154.5 \text{ kcal/mol} \qquad (7)$$

The driving force for all of these reactions is charge separation. Since neither CH_3^+ nor $C_2H_5^+$ have been observed directly in super acid media (although there is evidence for their intermediacy),[30] it seems quite impossible that $C_2H_4^{2+}$ could be a viable chemical intermediate under such conditions. It will strip an electron or an atom from an adjacent neutral (or negatively charged) species with avidity.

Fragmentation Barriers. While **1** is calculated to be a minimum on the potential energy surface, the $C_2H_4^{2+}$ dication is not likely to be more than a transient species unless reasonably large barriers to the various possible fragmentations (eq 2–4) are present.

The transition structure **6** for proton loss from **1** (with a C–H distance of 2.791 Å for the dissociating bond) was found to be 82.5 kcal/mol (6-31G** + ZPE) above the minimal $C_2H_4^{2+}$ energy. Electron correlation makes a large contribution and lowers the deprotonation barrier to 68.8 kcal/mol at the MP3 level. The size of this effect suggests that optimization with inclusion of

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(25) For example, see: (a) CH_6^{2+} and $C_2H_6^{2+}$, ref 1b, d. (b) CH_5^+, $C_2H_3^+$, $C_2H_5^+$, $C_2H_7^+$, and $C_3H_7^+$: Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. (c) $C_3H_4^{2+}$: Clark, T.; Weiss, R. *J. Org. Chem.* **1980**, *45*, 1790.

(26) Apeloig, Y.; Clark, T.; Kos, A. J.; Jemmis, E.; Schleyer, P. v. R. *Isr. J. Chem.* **1980**, *20*, 43.

(27) The MP3/6-31G**//6-31G* energies for the bridged vinyl cation, $C_2H_3^+$ (−77.35246 au) CH_3^+ (−39.36450 au), and the methine cation, CH^+ (−37.98749), were taken from ref 1a. The corresponding energy of the methylene radical cation, CH_2^+, is −38.66445 au.

(28) Lossing, F. P. *Can. J. Chem.* **1971**, *49*, 357; **1972**, *50*, 3973. Reinke, D.; Kraessig, R.; Baumgärtel, H. Z. *Z. Naturforsch. A* **1973**, *28A*, 1021. Polley, C. W.; Munson, B. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 49.

(29) McCulloh, K. E.; Dibeler, V. H. *J. Chem. Phys.* **1976**, *64*, 4445.

(30) Olah, G. A.; DeMember, J. R.; Schlossberg, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 156.

correlation corrections might lower the barrier further.[25b] Even taking the value of 68.8 kcal/mol as an upper limit, the barrier for proton loss is sizable. The value is comparable to the calculated barrier of 65.0 kcal/mol (MP4SDQ/6-31G** + ZPE) for proton loss from the triplet acetylene dication; the calculated transition structure for this latter process also has a long distance (2.707 Å, 6-31G*) for the fragmenting C–H bond.[1c]

The dissociation investigated for 4 is C–C bond cleavage to give the methyl and methine cation (eq 4). At MP3/6-31G*//6-31G* + ZPE, the transition structure **7** is 64.1 kcal/mol higher in energy than **4** and 85.4 kcal/mol higher than **1**. The relative effect of electron correlation on **7**, in contrast to **4**, is only small. The dissociating C–C bond in **7** has a length of 1.950 Å (6-31G*), an increase of 0.641 Å from **4**.

The third dissociation process is homolytic cleavage of **1** into two $CH_2^{+\cdot}$ radical cations (eq 3), which we calculated within D_{2d} symmetry constraints (structure **9**). Restricted Hartree–Fock (RHF) theory is inappropriate for describing this dissociative reaction coordinate, since singlet **1** is converted into two $CH_2^{+\cdot}$ doublets. Accordingly, we used unrestricted Hartree–Fock (UHF) theory, with an equal number of α and β electrons ($S_z = 0$), to allow one electron to go to each end of the breaking bond. At this UHF/3-21G level, fragmentation of **1** into two methylene cations has a barrier of 62.1 kcal/mol. Addition of electron correlation (MP3/6-31G**//3-21G) raises this to 88.4 kcal/mol. This high value, close to the C–C bond dissociation energy of ethane, demonstrates that electrostatic repulsion does not always lead to a reduction of fragmentation barriers.

Isoelectronic Comparisons. The $C_2H_4^{2+}$ dication is isoelectronic with the CBH_4^+ cation and neutral species with the composition $CBeH_4$ and B_2H_4. The experimentally still elusive diborane (4) provides the closest analogy. The potential energy surface of B_2H_4 has been well explored.[14] Bridged forms are not competitive and the global minimum has D_{2d} symmetry (like **1**). The calculated $H_2B–BH_2$ rotational barrier ($D_{2d} \rightarrow D_{2h}$) is rather insensitive to the level of theory employed: e.g., 12.2 kcal/mol at 3-21G//3-21G and 10.5 kcal/mol at 6-31G*//6-31G*[24] vs. 11.9 kcal/mol found by Vincent and Schaefer[14i] with electron correlation in the highest level study reported to date. Double hyperconjugation again favors the perpendicular (D_{2d}) form.[13] The B–B bond lengthening (0.078 Å, $D_{2d} \rightarrow D_{2h}$) compares with the C–C elongation, 0.155 Å, in $C_2H_4^{2+}$ (**1** → **2**). The rotational barrier is also about twice as large in the carbodication.

In this respect, the boron-stabilized methyl cation, $H_2B–CH_2^+$,[15] behaves similarly. The rotational barrier from the perpendicular (C_{2v}) to the planar (C_{2v}) form is 20.1 kcal/mol both at 4-31G//STO-3G and at 3-21G//3-21G;[24] the C–B bond lengthening at the latter level, 0.168 Å, is even greater than in the isoelectronic carbodication. However, unlike $C_2H_4^{2+}$ (**1**), the perpendicular $H_2B–CH_2^+$ geometry is not the most stable and it is not even a local minimum.[15b] Rearrangement to $H_3C–BH^+$ (akin to **4**) occurs without activation and releases 37.9 kcal/mol of energy (MP4/6-31G*//3-21G with ZPE correction). The formal charge is better located on the more electropositive boron atom.

The same structural preference is shown by methylberylium hydride,[31] $H_3C–BeH$. In effect, the doubly charged carbon in **4** is replaced by the isoelectronic Be. The isomeric structure, $H_2C^+–BeH_2^-$, can be viewed as a beryllium ylide. However, the perpendicular geometry gives one negative eigenvalue on diagonalization of the force constant matrix; this ylide is thus a saddle point 84.4 kcal/mol (3-21G//3-21G) above $H_3C–BeH$ in energy. Conversely, the boron ylide, $H_3B^-–BH^+$, is much less stable than the $H_2B–BH_2$ form.

Conclusions

The global and only $C_2H_4^{2+}$ energy minimum is indicated to be the perpendicular ethylene dication, **1**. The estimated $\Delta H_f{}^\circ{}_0(C_2H_4^{2+})$ is about 654 kcal/mol. The adiabatic double ionization of ethylene to give **1** is calculated to be 27.6 eV, and a value of 30.5 eV is obtained for the vertical process to give **3**.

The rotational barrier of the ethylene dication is 28.1 kcal/mol, while the isomerization to the ethylidene dication (itself presumably a transition structure) requires about 20 kcal/mol. Hydrogen scrambling in $C_2H_4^{2+}$ thus becomes effective at an excitation energy of about 1 eV.

The study indicates substantial kinetic stability for the $C_2H_4^{2+}$ dications. The deprotonation of the ethylene dication is exothermic by 16.4 kcal/mol, but has a large barrier of over 65 kcal/mol. The isothermal homolytic cleavage into two CH_2^+ cations may have an even larger barrier. We encourage further gas-phase experimental studies of ethylene, e.g., by mass spectroscopic charge stripping and charge separation techniques, in order to ascertain the accuracy of the calculational data.

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(31) $E(CH_3BeH) = -54.51528$ au at 3-21G//3-21G, ref 24.