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Structures and Energies of Isomeric $C_3H_6^{2+}$ Dications

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Abstract: The $C_3H_6^{2+}$ potential energy surface was studied by ab initio molecular orbital theory employing the 3-21G and 6-31G* basis sets and Møller-Plesset perturbation theory. The protonated allyl cation **1**, which formally has two terminal cation centers, and the propylidene dication **3**, which has formally both charges located at its central dimethyl-substituted carbon, have virtually the same energy at MP4/6-31G*. The relative high stability of these two isomers results from effective bishyperconjugation and crosshyperconjugation, respectively. Examples of [1,3]-H and [1,2]-CH_4 sigmatropic shifts are discussed for isomeric propylene and vinyl-substituted methonium diions; a transition structure with carbon hexacoordination is involved. Both dications **1** and **3** are predicted to be observable in the gas phase. Energy evaluations are presented for the adiabatic (di)oxidations from neutral and radical cation precursors.

Carbodications are increasingly common, both as species observable in solution and in the gas phase.[1,2] Exciting structures are exhibited by dications in super acid media; the dehydroadamantdiyl,[3] pagodane,[4] and Hogeveen dications[5] are illustrative. Their structures exemplify the special stabilizing properties (often uniquely) to doubly charged hydrocarbons. In contrast, structural and energetic information is very limited for the numerous doubly charged species that are now frequently observed in the gas phase.[2] However, with the rapid advance in theoretical dication studies such aspects are not only addressed, but also trends in behavior are established.[6] As part of our general investigation of such species,[7] we now report results on the $C_3H_6^{2+}$ potential energy surface. New bonding features are discussed that are characteristic of dications in general.

$C_3H_6^{2+}$ dications have been generated from several precursor molecules by charge-stripping mass spectroscopy,[8] but the detailed information is limited. The second ionization potential was reported to be 18.2 eV.[8b] March[8a] concludes that the $C_3H_6^{2+}$ is likely to have a cyclic structure on the basis of charge separation spectra. The generally high abundance of $C_nH_6^{2+}$ dications in charge exchange mass spectra has led to the suggestion that such species may possess a common $CH_3–C_{(n-2)}–CH_3^{2+}$ structural type.[2d] However, theoretical investigations indicate more complex geometries to be lower in energy for $n > 3$.[7j,k] In the present study we evaluate such dications for $n = 3$ and make comparisons with the experimental data. Relationships with the cyclopropyl and propene radical cations[9] will also be drawn.

Attempts to synthesize stabilized derivatives of $C_3H_6^{2+}$ in superacid media have failed.[10] This is in contrast to the success achieved in preparing dications with a two-carbon-unit separation between the charged centers and with substituted ethylene dications, where delocalization stabilizes the cation centers, which are formally adjacent to one other.[1,10] Nevertheless, the dioxidation of a 1,3-dihalide, yielding an allyl cation, and the diprotonation of a 1,3-diol, resulting in disproportionation, indicate the possible transient formation of a derivative of the $C_3H_6^{2+}$ dication.[10]

Table I. Total (in au) and Relative (in kcal/mol) Energies of $C_3H_6^{2+}$ Isomers

	HF/3-21G[a]		HF/6-31G*[a]	
structures	abs	rel	abs	rel
1, C_{2v}	−115.56665	0.0 (0)	−116.22307	0.0 (0)
2, C_s	−115.55542	7.0 (1)	−116.21298	6.3 (1)
3, D_{3d}	−115.51916	29.8 (0)	−116.17006	33.3 (0)
4, D_{3h}	−115.51904	29.9 (1)	−116.16985	33.4 (1)
5, C_s	−115.53278	21.3 (0)	−116.19075	20.3 (1)
6, C_s	−115.50140	40.9 (1)	−116.16145	38.7 (2)
7, C_{2v}	−115.49288	46.3 (1)	−116.16476	36.6 (1)
8, C_s	−115.47888	55.1 (0)	−116.13405	55.9 (0)
9, C_{2v}	−115.47489	57.6 (1)	−116.12467	61.7 (1)
10, C_s	−115.41527	95.0 (1)	−116.08273	88.1 (1)
11, C_1	−115.47234	59.2 (0)	−116.13092	57.8 (0)
12, C_s	−115.47126	59.9 (1)	−116.13003	58.4 (1)
13, C_{2v}	−115.49353	45.9 (1)	−116.15192	44.6 (1)
13t, D_{3h}	−115.42735	87.4 (0)		
14, C_2	−115.47655	56.5 (2)		
15, C_{2v}	−115.36218	128.3 (2)		
16, C_{2v}	−115.11241	285.0 (3)		
17, C_{3v}	−115.17187	247.7 (4)		

[a] Values in parentheses indicate the number of imaginary frequencies.

Rearrangements of carbodications have received little attention other than the possibility that the same processes familiar in monocation chemistry occur. While similarities may be expected, carbodication rearrangements may proceed via unfamiliar transition structures. We demonstrate this by [1,3]-H and [1,2]-methonium shifts. Conceptually, dication structures can be composed from smaller fragments using a building block approach. This approach has helped to explain why dications often have geometries very different from those of their neutral homologues. For example, the methane dication, CH_4^{2+}, a hydrogen-complexed methylene dication,[7a,l] and the carbenium–carbonium ethane dication, $CH_4–CH_2^{2+}$,[7c] exemplify such different types of structural

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Table II. Total (in au) and Relative (in kcal/mol) MP/6-31G* Energies of $C_3H_6^{2+}$ Isomers

structures	MP2 abs	MP2 rel	MP3 abs	MP3 rel	MP4 abs	MP4 rel	MP4 + ZPE rel
1,[a] C_{2v}	−116.53940	0.0	−116.57610	0.0	−116.59122	0.0	0.0
2, C_s	−116.52856	6.8	−116.56538	6.7	−116.58081	6.5	6.5
3,[a] D_{3d}	−116.53334	3.8	−116.56012	10.0	−116.58629	3.1	−0.8
4, D_{3h}	−116.53306	4.0	−116.55989	10.2	−116.58604	3.3	−0.7
5, C_s	−116.51734	13.8	−116.55209	15.1	−116.57047	13.0	11.8
6, C_s	−116.49025	30.8	−116.52520	31.9	−116.54451	29.3	27.7
7, C_{2v}	−116.51028	18.3	−116.54194	21.4	−116.56073	19.1	18.0
8, C_s	−116.48694	32.9	−116.51851	36.1	−116.53963	32.4	29.7
9, C_{2v}	−116.48447	34.4	−116.51520	38.2	−116.53597	34.6	29.3
10, C_s	−116.45386	53.7	−116.48049	60.0	−116.50117	56.5	53.9
11, C_1	−116.48524	34.0	−116.51712	37.0	−116.53702	34.0	32.0
12, C_s	−116.48499	34.1	−116.51691	37.1	−116.53667	34.2	32.0
13, C_{2v}	−116.47639	39.6	−116.51201	40.2	−116.52876	39.2	39.5

[a] The energy difference between the MP2/6-31G* optimized structures **1** and **3** is 3.4 kcal/mol. At this level the total energy of **1** is −116.55438 au.

organization. Adiabatic dioxidation of hydrocarbons often have anti-van't Hoff geometries as exemplified in the $H_2C_nH_2$ series, the planar CH_4^{2+}, perpendicular $H_2CCH_2^{2+}$, and cummulene-type dications ($n = 3$ and higher).[2] The various $C_3H_6^{2+}$ isomers explored in the present paper broaden the scope of structural recognition for dications in general.

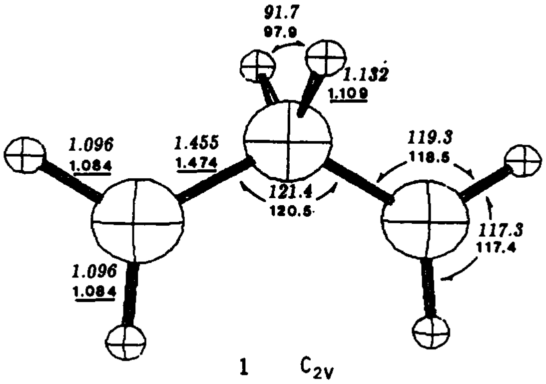
Computational Methods

Ab initio molecular orbital calculations[11] were performed with the GAUSSIAN 82 and 86 series of programs[12] using the gradient geometry optimization[13] and standard basis sets.[14] Singlets were calculated by the restricted Hartree–Fock (RHF) approximation[15a] and triplets by the unrestricted version (UHF).[15b] All geometries were fully optimized using first the split-valence 3-21G[14a] and then the d-polarized 6-31G*[14b] basis sets. The effect of valence electron correlation corrections was investigated with Møller-Plesset perturbation theory to full fourth order,[16] which includes single, double, triple, and quadruple substitutions (denoted MP4/6-31G*//HF/6-31G*, where "//" means "at the geometry of"). The influence of electron correlation at MP2 was explored in the 6-31G* geometry optimization of structures **1** and **3**. The force constant matrices were constructed for all geometries to verify whether they are minima, saddle points, or points of higher order on both the 3-21G and 6-31G* potential energy surfaces; equilibrium structures have no negative eigenvalues, while transition structures have one. Some higher order stationary points were also encountered.

Results and Discussion

Absolute, relative Hartree–Fock (HF/3-21G and HF/6-31G*), and correlated (MP4/6-31G*) energies for all structures are summarized in Tables I and II. ORTEP diagrams of the HF/6-31G* geometries are displayed throughout the text with MP2/6-31G* geometrical parameters for **1** and **3** given in italics. Also included in Table I are the number of imaginary frequencies obtained at the Hartree–Fock level. The 6-31G* frequencies and zero-point vibrational energies (ZPE) are listed in Table III. Four 6-31G* minima and seven saddle points were determined. Characterization of these stationary points at 3-21G is similar, but there are some exceptions. Unless otherwise noted, 6-31G* geometries and MP4/6-31G* + scaled[17] ZPE relative energies (listed in Table II) are discussed below. The computational results for the various $C_3H_6^{2+}$ isomers are considered first in terms of structural types, followed by energy and stability evaluations.

Protonated Allyl Cation. Structure **1** with C_{2v} symmetry is the global $C_3H_6^{2+}$ dication minimum at MP4/6-31G*, although in-



1 C_{2v}

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Table III. HF/6-31G* Harmonic Frequencies of $C_3H_6^{2+}$ Isomers

structures	frequencies	ZPE
1, C_{2v}	241 (b$_1$), 287 (a$_2$), 445 (a$_1$), 590 (b$_1$), 940 (a$_1$), 987 (b$_2$), 1094 (b$_2$)	
	1122 (a$_2$), 1211 (a$_1$), 1348 (a$_1$), 1386 (b$_1$), 1456 (a$_2$), 1532 (b$_2$), 1632 (a$_1$)	
	1637 (b$_2$), 3014 (a$_1$), 3015 (b$_1$), 3280 (b$_2$), 3283 (a$_1$), 3401 (b$_2$), 3405 (a$_1$)	50.5
2, C_s	−314 (a$''$), 199 (a$''$), 387 (a$'$), 705 (a$''$), 914 (a$'$), 1041 (a$'$), 1074 (a$'$)	
	1128 (a$'$), 1319 (a$''$), 1356 (a$'$), 1439 (a$'$), 1442 (a$''$), 1536 (a$'$), 1619 (a$'$)	
	1630 (a$'$), 3054 (a$'$), 3096 (a$''$), 3277 (a$'$), 3280 (a$'$), 3403 (a$'$), 3403 (a$''$)	50.5
3, D_{3d}	65 (a$_{1u}$), 318 (e$_u$), 318 (e$_u$), 665 (e$_g$), 665 (e$_g$), 906 (a$_{1g}$), 980 (e$_u$)	
	980 (e$_u$), 1300 (e$_g$), 1300 (e$_g$), 1334 (e$_u$), 1334 (e$_u$), 1357 (a$_{2u}$), 1406 (a$_{1g}$)	
	1565 (a$_{2u}$), 2879 (a$_{2u}$), 2951 (a$_{1g}$), 2968 (e$_u$), 2968 (e$_u$), 2981 (e$_g$), 2981 (e$_g$)	46.1
4, D_{3h}	−64 (a$_1''$), 336 (e$'$), 336 (e$'$), 600 (e$''$), 600 (e$''$), 907 (a$_1'$), 1060 (e$'$)	
	1060 (e$'$), 1249 (e$''$), 1249 (e$''$), 1354 (e$'$), 1354 (e$'$), 1357 (a$_2''$), 1408 (a$_1'$)	
	1563 (a$_2''$), 2880 (a$_2''$), 2952 (a$_1'$), 2963 (e$''$), 2963 (e$''$), 2988 (e$'$), 2988 (e$'$)	46.0
5, C_s	−36 (a$''$), 317 (a$'$), 487 (a$''$), 727 (a$''$), 873 (a$'$), 921 (a$''$), 1030 (a$'$)	
	1111 (a$'$), 1211 (a$''$), 1290 (a$'$), 1359 (a$'$), 1447 (a$'$), 1482 (a$''$), 1517 (a$'$)	
	1585 (a$'$), 3015 (a$'$), 3038 (a$''$), 3144 (a$'$), 3176 (a$'$), 3264 (a$''$), 3354 (a$'$)	49.1
6, C_s	−519 (a$''$), −170 (a$''$), 425 (a$'$), 706 (a$''$), 795 (a$'$), 949 (a$''$), 1000 (a$'$)	
	1128 (a$'$), 1215 (a$'$), 1335 (a$''$), 1372 (a$'$), 1407 (a$''$), 1490 (a$'$), 1586 (a$'$)	
	1653 (a$'$), 2818 (a$''$), 2863 (a$'$), 3249 (a$'$), 3333 (a$'$), 3361 (a$'$), 3387 (a$'$)	48.7
7, C_{2v}	−293 (b$_2$), 572 (b$_1$), 721 (a$_1$), 788 (a$_2$), 815 (b$_1$), 988 (b$_2$), 1155 (b$_1$)	
	1179 (a$_1$), 1231 (a$_2$), 1259 (b$_2$), 1397 (b$_1$), 1416 (a$_1$), 1437 (b$_2$), 1485 (a$_1$)	
	1733 (b$_2$), 2144 (a$_1$), 3120 (b$_2$), 3151 (a$_1$), 3246 (a$_2$), 3247 (b$_1$), 3314 (a$_1$)	49.2
8, C_s	288 (a$'$), 319 (a$''$), 387 (a$''$), 664 (a$''$), 733 (a$''$), 899 (a$'$), 958 (a$'$)	
	1091 (a$''$), 1102 (a$'$), 1169 (a$'$), 1395 (a$'$), 1453 (a$''$), 1496 (a$'$), 1626 (a$'$)	
	1934 (a$'$), 2053 (a$''$), 2986 (a$'$), 3124 (a$''$), 3128 (a$'$), 3164 (a$'$), 3251 (a$''$)	47.5
9, C_{2v}	−235 (a$_2$), −55 (b$_1$), 294 (b$_1$), 318 (b$_2$), 536 (b$_2$), 714 (b$_2$), 903 (a$_1$)	
	1079 (b$_1$), 1118 (b$_1$), 1136 (b$_2$), 1229 (a$_1$), 1382 (a$_2$), 1419 (a$_2$), 1438 (a$_1$)	
	1971 (a$_1$), 2646 (a$_1$), 2760 (a$_1$), 2852 (b$_2$), 2857 (b$_1$), 3161 (a$_1$), 3246 (b$_2$)	44.5
10, C_s	−577 (a$''$), 287 (a$''$), 573 (a$''$), 646 (a$'$), 783 (a$'$), 850 (a$'$), 852 (a$''$)	
	902 (a$'$), 1079 (a$'$), 1113 (a$''$), 1176 (a$'$), 1455 (a$'$), 1456 (a$''$), 1687 (a$'$)	
	2089 (a$''$), 2090 (a$'$), 3031 (a$'$), 3161 (a$''$), 3174 (a$'$), 3371 (a$''$), 3493 (a$'$)	47.6
11, C_1	132 (a), 318 (a), 644 (a), 724 (a), 772 (a), 891 (a), 920 (a)	
	993 (a), 1161 (a), 1239 (a), 1253 (a), 1469 (a), 1541 (a), 1682 (a)	
	1939 (a), 2236 (a), 2891 (a), 3135 (a), 3164 (a), 3233 (a), 3387 (a)	48.2
1i, C_s	−128 (a$''$), 336 (a$'$), 662 (a$''$), 706 (a$''$), 760 (a$''$), 853 (a$'$), 928 (a$'$)	
	1057 (a$''$), 1098 (a$'$), 1214 (a$'$), 1253 (a$'$), 1470 (a$''$), 1536 (a$'$), 1682 (a$'$)	
	1943 (a$'$), 2277 (a$''$), 2868 (a$'$), 3134 (a$'$), 3172 (a$'$), 3197 (a$''$), 3394 (a$'$)	48.0
13, C_{2v}	−642 (b$_2$), 337 (a$_2$), 555 (a$_1$), 784 (b$_1$), 802 (b$_2$), 902 (b$_1$), 1119 (a$_2$)	
	1240 (b$_1$), 1276 (a$_1$), 1335 (b$_2$), 1337 (a$_2$), 1422 (a$_1$), 1508 (a$_1$), 1573 (b$_2$)	
	1670 (a$_1$), 3174 (a$_1$), 3239 (b$_2$), 3256 (a$_1$), 3291 (b$_2$), 3364 (a$_2$), 3372 (b$_1$)	50.8

[a] Unscaled zero-point energies (ZPE) in kcal/mol. For relative energy corrections (see Table I) these ZPE values have been scaled by 0.89. See ref 34.

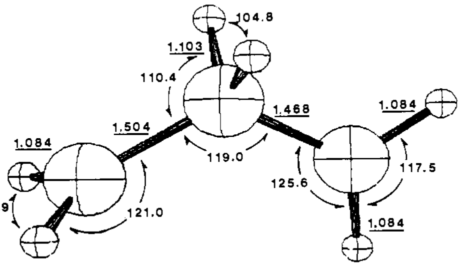
clusion of zero-point energies renders isomer **3** slightly more stable (Table II). Structure **1** is the parent, *gem*-dicarbinyl cation-substituted methane in which the two cationic units are formally separated by one CH_2 group.

The HF/6-31G* geometry of **1** shows a close resemblance to that of the allyl cation and suggests that **1** can be viewed as a centrally protonated allyl cation. Particularly impressive are the 11.0° widening of the CCC angle in **1** (to 120.5°) for the ideal tetrahedral angle and the corresponding 11.6° reduction in the central HC_2H angle to 97.9°. The CCC angle in the allyl cation is 119.5° (same level). The relatively short 1.474 Å C–C bond distances in **1** are also noteworthy, especially in light of charge–charge repulsion effects expected in dications. However, the allyl cation C–C bond lengths of 1.373 Å (HF/6-31G*) are 0.1 Å shorter.[18] The UHF/6-31G* geometry of the trimethylene radical cation (C_{2v})[9a] with C–C bond lengths of 1.433 Å and a CCC angle of 125.9° is also reminiscent of that of **1**. Although the radical cation is a UHF transition structure, MP2 calculations suggest this species to be a shallow minimum.[9a]

The short, 1.474 Å C–C bond lengths in **1** may be explained in terms of *bishyperconjugation, which is defined as the combined hyperconjugative effect on the same C–H bond(s) by two adjacent cation centers.*[9a] Such joint action enhances the π conjugative interaction between two geminal carbinyl cation groups. Inspection of the π MO (no. 10, HOMO-1) does indeed show bonding involving both CH_2^+ p_z orbitals and that of the central carbon (which, of course, also involves its hydrogens). The CC overlap popultion is 0.591. This C–C bond shortening, due to hyperconjugation, is accompanied by the widening of the CCC angle (120.5°), but charge–charge repulsion may also contribute.

Considering structure **1** as a CH_2^+-substituted ethyl cation, a comparison of **1** with the CC bond of the well-studied classical $C_2H_5^+$ cation is appropriate. (We recognize that the bridged form is more stable at post-Hartree–Fock levels.[18]) At 6-31G* CH_3–CH_2^+ in the staggered conformation has a C–C bond length of 1.432 Å and one elongated C–H bond of 1.115 Å.[18] The corresponding bond lengths in **1** are 1.474 and 1.109 Å, respectively. Thus, although hyperconjugation clearly is present in dication **1**, it is significantly less than in the classical ethyl monocation.

Rotating one of the carbinyl cation groups in **1** by 90° to give **2** disrupts the bishyperconjugative effect. Although both CH_2^+ groups can now interact separately with the central methylene unit, as is evident from the short C–C bonds of 1.468 and 1.504 Å, there is no formal conjugation among the three carbons. Even



2 C_s

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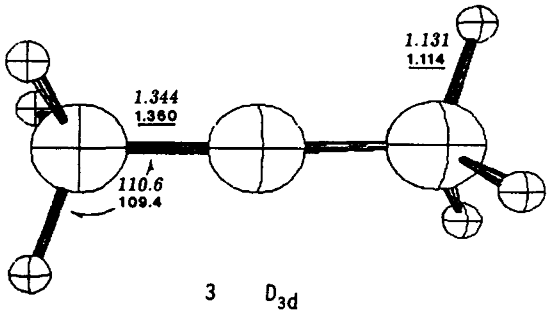
(18) (a) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. (b) Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Carnegie-Mellon University: Pittsburgh, PA, 1983. (c) Wong, M. W.; Baker, J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2245.

so, the CCC angle remains large (119.0°) and the central C–H bonds (1.103 Å) are elongated. However, the HCH angle of 97.9° in **1** widens to 104.8° (HF/6-31G*). The "rotated" CH_2^+ group in **2** is mainly involved hyperconjugatively with the perfectly aligned $C-CH_2^+$ bond, but is subject to electrostatic repulsion. Normal mode analysis of the imaginary frequency shows structure **2** to be a transition structure for rotation of a CH_2^+ group in **1**. The energy barrier for this CH_2^+ rotation (**1** → **2**) is 6.5 kcal/mol at MP4/6-31G*//HF/6-31G* + ZPE. Consequently, the extra stabilization resulting from bishyperconjugation involving the central CH_2 group is significant.

Besides diprotonation, many dications can also be viewed as complexes involving H_2.[2a,6] Typical examples are CH_4^{2+},[7l] CH_6^{2+},[7b] and the ethane dication,[7c] which possess 3c–2e bonds resulting from dication center–H_2 molecule interactions. The H–H distance in these species is ca. 0.9 Å. Although such an interaction between the allene dication (the global $C_3H_4^{2+}$ minimum)[20] and hydrogen could afford structure **1**, there is no evidence for a 3c–2e bond in **1**.

Electron correlation effects can influence geometrical parameters significantly. For example, at the MP2/6-31G* level the ethyl cation optimizes to a bridged species, while H_2-cation complexes become more stable.[18] Therefore, we optimized structure **1** at MP2/6-31G*. At this level, as compared with HF, the C–C bonds contract 0.019 to 1.455 Å, while the methylene C–H bonds elongate 0.022 to 1.131 Å, and the angle between them is reduced further by 6.2° to 91.7°. These changes suggest some tendency for formation of 3c–2e bonding in the methylene carbon, but the H–H separation is still 1.624 Å. However, the bishyperconjugative effect is clearly stronger at the correlated level.

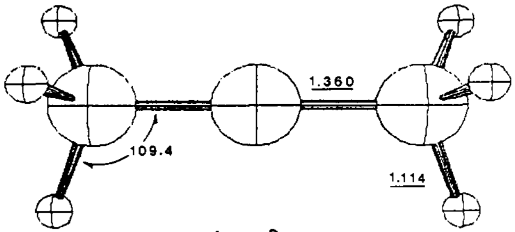
Propylidene Dication. The propylidene dication **3** (D_{3d}) is the second "best" $C_3H_6^{2+}$ isomer at MP2/6-31G*, but is favored over isomer **1** when zero-point energies are included (Table II). This equilibrium structure is the dimethyl derivative of the parent linear methylene dication[7a] CH_2^{2+} ($D_{\infty h}$). It also is the monomethyl derivative of CH_3-CH^{2+} (C_{3v}), a high-energy $C_2H_4^{2+}$ isomer, which has been subject of previous theoretical studies.[7c,21] Structure **3** displays interesting geometrical features. The C–C bonds to the divalent carbodication center (1.360 Å) are quire short and are nearly equal in length to C=C double bonds (!). This suggests cummulenic bonding, although the C–C lengths in allene (1.23 Å at 6-31G*) is significantly shorter.[22] All C–H bonds in **3** are correspondingly long, 1.114 Å, despite the nearly perfect tetrahedral arrangements of the terminal carbons (∠CCH = 109.4°). The MO's of **3** clearly show the expected conjugation in the two orthogonal π planes. The overlap population analysis shows significant transfer of positive charge from the carbon dication center to all hydrogens.



3 D_{3d}

As in **1**, much of the stabilization of structure **3** results from hyperconjugation. However, in contrast to **1**, *the hyperconjugation in* **3** *occurs in two orthogonal planes. We have termed this crosshyperconjugation.*[19] Previously, this effect was described in $C_2H_4^{2+}$ structures;[7c] the ethylene dication (D_{2d}) and its higher energy ethylidene dication isomer (C_{3v}) both display very short C–C bonds, 1.400 and 1.297 Å (MP2/6-31G*), respectively.[21a]

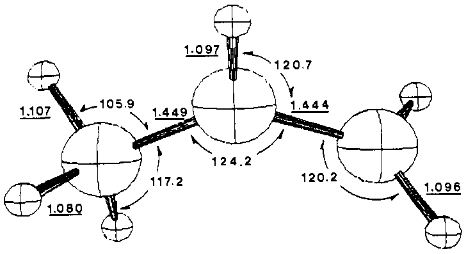
Whereas the magnitude of the stabilization resulting from crosshyperconjugation may be estimated by rotating around the C–C bond in the ethylene dication ($D_{2d} - D_{2h}$), such rotations have 6-fold periodicity and have little effect in the propylidene dication (**3**). The latter has two orthogonal p orbitals on the central carbon, and hyperconjugative interaction with the terminal methyl group hydrogens is maintained during rotation. In contrast, this effect is "turned off" by rotation in doubly ionized ethylene. Consequently, the geometry of the propylidene dication transition structure **4**, with D_{3h} symmetry, is virtually the same as that for **3**. The barrier for C–C bond rotation in **3** is less than 0.1 kcal/mol (MP4/6-31G* + ZPE)! A similar situation is found in dimethylacetylene.[18b]



4 D_{3h}

Because of the sensitivity of hyperconjugative interactions to electron correlation effects, we optimized structure **3** at MP2/6-31G*. Expectantly, both C–C bonds decrease in length by 0.016 Å to an impressively short 1.344 Å, whereas all six C–H bonds lengthen to 1.131 Å.

Propylene Dication. Adiabatic (di)oxidation of propylene or its radical cation may afford dication **5** (C_s). Unlike propylene, the neighboring trivalent cation centers in **5** are orthogonal to each other as in the parent ethylene dication $C_2H_4^{2+}$ (D_{2d}). As in **1** and **3**, hyperconjugation also is important in **5**. The C–C bond length between the two formally charged carbons is only 1.444 Å (versus 1.318 Å in propylene[18] and 1.432 Å in the D_{2d} ethylene dication,[7c] both also at HF/6-31G*). Hence, **5** also is subject to strong crosshyperconjugation, resulting from interaction of two formally vacant orthogonal orbitals with the vicinal CH_2 groups. The positive charge is delocalized further by hyperconjugative stabilization involving the methyl group; this is evident from the short methyl C–C bond length of 1.449 Å (virtually the same as that of the C^+-C^+ bond). The CH_3-C bond is shortened by 0.054 Å from neutral propylene! The propylene radical cation, which is the global minimum at UHF/6-31G*, has C–C bond lengths of 1.408 and 1.472 Å. Although **5** is an equilibrium structure at 3-21G, it represents a saddle point at HF/6-31G*. Analysis of the normal mode of the very small imaginary frequency (36i cm^{-1}) indicates **5** to be a transition structure for methyl group rotation. However, because of the expected small gain in stabilization (see the discussion on **3**), this species with C_1 symmetry was not pursued further.



5 C_s

Rotation around the C^+-C^+ bond in **5** to yield structure **6** has a significant influence on the geometry. Because of the absence of crosshyperconjugation and the enhanced repulsion between the eclipsed bonds of the in-plane trivalent centers, the C–C bond

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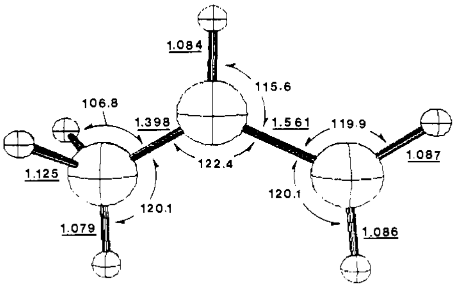
[19] Lammertsma, K. 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept 1986; Paper ORGN 25.

[20] Schleyer, P. v. R.; Lammertsma, K., unpublished results.

[21] (a) Wong, M. W.; Yates, B. F.; Nobes, R. N.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 3181. (b) Nobes, R. N.; Wong, M. W.; Radom, L. *Chem. Phys. Lett.* **1987**, *136*, 299. (c) Dewar, M. J. S.; Reynolds, C. H. *THEOCHEM* **1986**, *136*, 209.

[22] Rauk, A.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1985**, *107*, 3780.

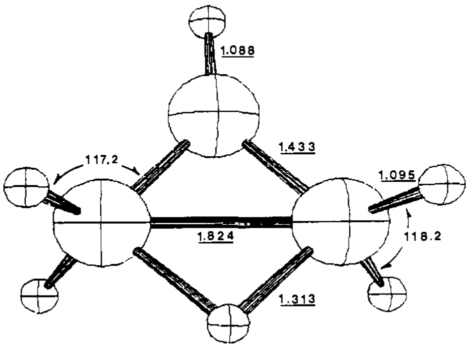


6 C_s

length increases by 0.117 to 1.561 Å. For comparison, the parent planar ethylene dication (D_{2h}) has a C–C bond length of 1.587 Å (same level).[7e] While the C–C rotational barrier in the ethylene dication is 28.1 kcal/mol (MP3/6-31G**//HF/6-31G* + ZPE),[7e] this rotation in the propylene dication, 5 → 6, is reduced to 15.9 kcal/mol (MP4/6-31G*//HF/6-31G* + ZPE) due to methyl hyperconjugation. This stabilization is stronger in 6 than in 5, as is shown by the different C–C bond lengths of 1.398 and 1.449 Å, respectively, and the two elongated methyl C–H bonds (1.125 Å). Similar to 5, structure 6 also has an imaginary frequency (173i cm^{-1}, HF/6-31G*) for CH_3 rotation.

Sigmatropic Shifts. Hydrogen, methyl, and phenyl [1,2] shifts are characteristic of carbocation chemistry.[23] These are the important processes through which many cations rearrange to thermodynamically more stable isomers. The [1,2] shifts have attracted significant attention in the context of "classical" (or localized) versus "nonclassical" (or bridged) cations as exemplified by the discussion on the norbornyl cation.[24] We already referred to the parent ethyl cation, $C_2H_5^+$, which favors a bridged (3c-2e) structure at post-Hartree–Fock levels;[18] supporting experimental evidence is available.[25] Extensive ^1H and ^{13}C NMR studies in solution under stable ion conditions have revealed many details concerning the nature of the species involved in formal [1,2] shifts in cations.[23] In contrast, little is known about sigmatropic shifts in doubly charged species.

While [1,2]-H shifts take place in monocations, a [1,3]-H shift must occur in the corresponding dication to satisfy a two-electron pericyclic process. Just as the bridged ethyl cation $C_2H_5^+$ exemplifies a "frozen" [1,2] shift in a singly charged system, the propylene dication $C_3H_6^{2+}$ (7) represents the parent for a [1,3] shift in a doubly charged system. Structure 7 describes the saddle point for the degenerate [1,3]-H transfer in the propylene dication 5 (a ($2\sigma_s + 0\pi_s$) allowed process), as is evident from the normal mode of its imaginary frequency (293i cm^{-1} (b_2)). The barrier for this process (5 ⇌ [7] ⇌ 5) is 6.2 kcal/mol (MP4/6-31G* + ZPE). Although higher levels of theory (e.g., with inclusion of H-polarization and electron correlation in the geometry optimization) may modify this value, 7 is likely to remain a transition structure. Because of the 1.824 Å distance between the "terminal" carbons and the 1.313 Å long μ-hydrido bonds, structure 7 may alternatively be viewed as a side-protonated cyclopropyl cation.



7 C_{2v}

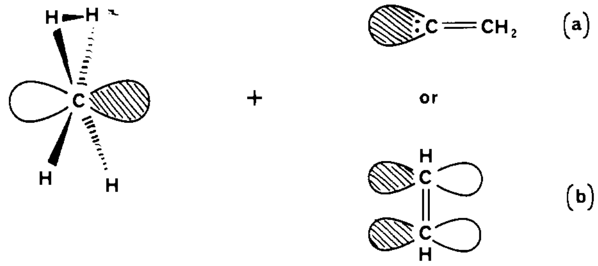
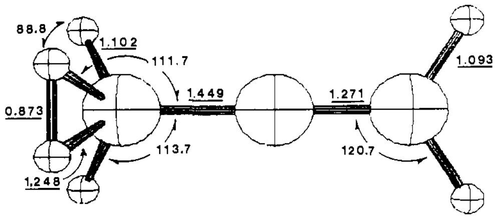


Figure 1. Schematic presentation of the CH_4^{2+} acceptor with (a) vinylidene and (b) acetylene donors.

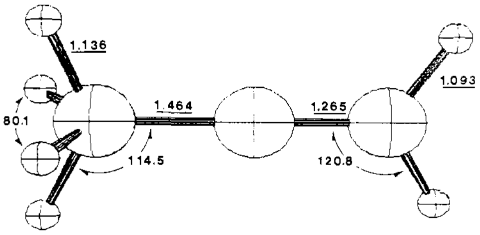
Substituted Methonium Ions. Carbodications can possess hypercoordinated carbons. Hexacoordination is illustrated by the parent CH_6^{2+}[7b] and by the Hoogeveen dications,[5] $(CR)_6^{2+}$ (R = H, CH_3, and C_2H_5). Various doubly charged species containing a pentacoordinate methonium group have also been studied computationally.[7f,21a] The ethane dication, CH_4^+–CH_2^+, a carbonium–carbenium diion, is noteworthy.[7c,g,20] Such species can be considered to be cation-substituted methonium ions, CH_4^+–R^+, possessing a 3c-2e CHH bond.[7f] A building-block approach can be used to rationalize the unusual geometrical features of carbodications.[2a,6] With respect to $C_3H_6^{2+}$ the feasible combinations are CH_4^{2+} with (a) vinylidene and (b) acetylene (see Figure 1).

α-Methonium Vinyl Dication. The β-vinyl substituted methonium ion 8 is an equilibrium structure 32.4 kcal/mol (MP4/6-31G*) less stable than, 1, and can be constructed from CH_4^{2+} and :C=CH_2. In this formalism the vinylidene's lone pair interacts with the empty p orbital of the planar methane dication. A σ bond results and positive charge transfers to the β-vinyl carbon with concomitant formation of a 3c-2e CHH bond (H-H = 0.873 Å) on the electron-accepting carbon. The orthogonality of this CHH bond to the empty p orbital of the central carbon in 8 causes maximization of the crosshyperconjugative effect along the carbon chain. This is evident from both the short 1.449 Å C–C single bond (despite formal charge–charge repulsion on neighboring carbons) and the short 1.271 Å C=C double bond. The one carbon smaller ethane dication, CH_4^+–CH_2^+, has a slightly longer C–C single bond of 1.466 Å (MP2/6-31G*).[20] While this latter $C_2H_6^{2+}$ structure has been regarded as a hydrogenated ethylene dication complex, H_2–$C_2H_4^{2+}$, also 8 can be viewed as a hydrogen complex of the planar allene dication $C_3H_4^{2+}$ (D_{2h}), which has anti-van't Hoff geometry.



8 C_s

We also investigated 9 (C_{2v}) for comparison with the (C_{2v}) ethane dication, which has local C_{4v} symmetry for the CH_4^+ group



9 C_{2v}

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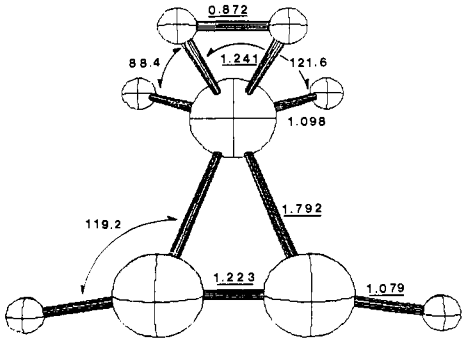
(23) Vogel, P. *Carbocation Chemistry*; Elsevier: New York, 1985.

(24) Montgomery, L. K.; Grendze, M. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4749.

(25) (a) Dyke, J. M.; Ellis, A. R.; Keddar, N.; Morris, A. *J. Phys. Chem.* **1984**, *88*, 2565. (b) Baer, T. *J. Am. Chem. Soc.* **1980**, *102*, 2482. (c) Houle, F. A.; Beauchamp, J. L. *Ibid.* **1979**, *101*, 4067.

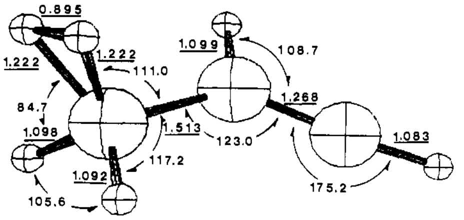
and is less stable than the $C_2H_6^{2+}$ isomer discussed above.[7g] Structure **9** with the four C–H bonds of the CH_4^+ group pairwise equivalent (1.135 and 1.137 Å) has one imaginary HF/6-31G* frequency and represents the transition structure for rotation of the CH_4^+ hydrogens in **8**. The diminished conjugation in structure **9** versus **8** is reflected in the 2.3 kcal/mol (MP4/6-31G* + ZPE) energy difference.

Degenerate β-Methonium Vinyl Cations through Hexacoordination. Ring structure **10** (C_s) contains one hexacoordinated and two tricoordinated carbons. This unusual dication can be regarded to arise from the formal interaction of the empty p orbital of planar CH_4^{2+} with an acetylene π bond. Similar to the parent CH_6^{2+} dication,[7b] the hexacoordinated carbon in **10** also possesses two 3c–2e interactions, one of which is a CCC ring. The CHH three-center bond has typical short H–H (0.872 Å) and long C–H (1.241 Å) distances. The 3c–2e CCC interaction results in a very short distal C–C bond length of 1.223 Å. This and the hydrogen deviation of only 9.2° from linearity are indicative of triple bonding. The weak interactions (C–C = 1.792 Å) to the apical hexacoordinated carbon are apparent.



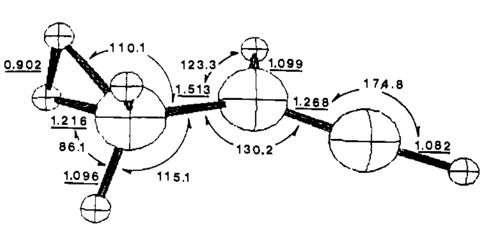
10 C_s

Isomer **10** has one imaginary frequency and represents the symmetrical transition structure for the *degenerate* [*1*,*2*]-*methonium transfer* over an acetylene unit. This resembles the [1,2]-H transfer in the vinylidene $C_2H_3^+$ monocation, where the bridged geometry species represents the minimum energy structure.[18] The methonium ion substituted vinyl cation **11** (C_1) is the minimum energy isomer associated with transition structure **10**. The energy barrier for this degenerate rearrangement (**11** ⇌ [**10**] ⇌ **11**) is 21.9 kcal/mol (MP4/6-31G* + ZPE). Higher level calculations are not expected to modify this value significantly.



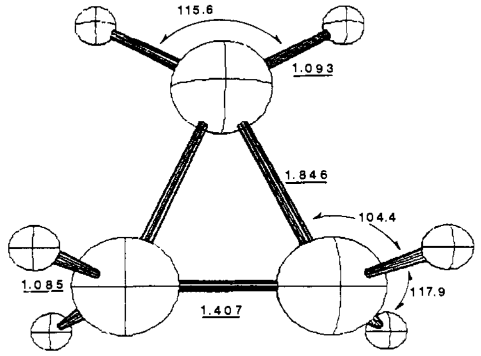
11 C_1

Many of the geometrical parameters of **11** compare with those of **8**. The longer C–CH_4^+ bond length in **11** of 1.513 Å versus 1.449 Å in **8** results from lack of crosshyperconjugation; the cationic centers in **11** are separated by one carbon unit, whereas they are adjoining in **8**. Structure **11** lacks symmetry due to π-overlap maximization of the methonium 3c–2e CHH interaction with the olefinic bond. Rotation of this CH_4^+ group, so that the CHH ring is intersected by the adjacent vinyl C–H bond, gives structure **12** (C_s), which is the transition structure for the methonium group rotation in **11**. Expectantly, the barrier for this process is very small, i.e., less than 0.1 kcal/mol (MP4/6-31G* + ZPE); rotations of CHH three-center bonds in CH_5^+ and CH_6^{2+} are of similar small magnitude.[18,7b] The energy difference between the two vinyl dication derivatives **8** and **11** is very small and amounts to only 2.3 kcal/mol in favor of **8**. Both structures are significantly higher in energy than **1**, which is stabilized by 29.7 kcal/mol over **8** (MP4/6-31G* + ZPE).



12 C_s

Cyclopropane Dication. Dioxidized hydrocarbons can be expected to have structures different from their neutral analogues.[2a,6] For example, the $C_nH_4^{2+}$ species have anti-van't Hoff geometries.[7k] The planar methane dication is the smallest of these, but also larger systems as the spiropentadiene dication fall into this class. Dioxidized cyclopropane is no exception as is shown by structure **13** (C_{2v}). This species has a planar tetracoordinate carbon in a three-membered C-ring. Cyclopropane has a degenerate HOMO. Removal of two electrons from one orbital results in Jahn–Teller distortion and hence major structural changes. Even though triplet structure **13t** is a minimum (UHF/3-21G), it is not competitive energetically and was not investigated further. Interestingly, all C–C bonds in **13** (1.407 and 1.486 Å) are significantly shorter than those in cyclopropane;[18] again, removal of electrons contracts the geometry. Structure **13** can also be considered as a composition of the building blocks CH_2^{2+} ($D_{\infty h}$, empty p orbital) and ethylene (D_{2h} 2π electrons). However, instead of being a minimum, dication **13** is transition structure for C-scrambling in **1**. The energy difference between **1** and **13** amounts to 39.5 kcal/mol (MP4/6-31G* + ZPE).

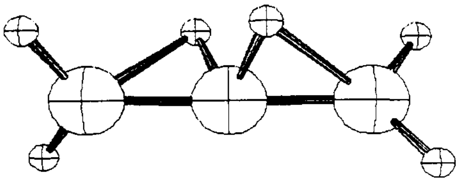


13 C_{2v}

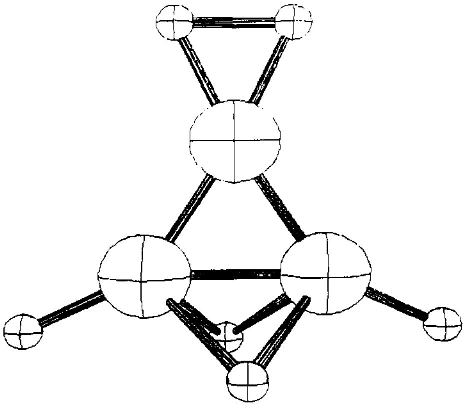
Other Structures. A variety of $C_3H_6^{2+}$ structures, like **14**, **15**, **16**, and **17** ("Ottoman crown"), were explored at HF/-3-21G. None of these were favorable energetically and all had multiple imaginary frequencies. Particular attention was paid to **14**, as this structure might represent the transition between **1** and **3**. This μ-dihydrido bridged isomer was obtained by enforcing linearity of the C-chain in the geometry optimization. However, the two imaginary HF/3-21G frequencies proved **14** to be a stationary point of second order.

Relative Stabilities. The four HF/6-31G* equilibrium structures are **1**, **3**, **8**, and **11**, with a fifth resembling **5**. At this Hartree–Fock level, **1** is significantly more stable than all other isomers; the smallest energy difference is 33.3 kcal/mol with **3**. The near-similarity of HF/3-21G and HF/6-31G* relative energies shows that for the $C_3H_6^{2+}$ isomers addition of d-polarization functions does not stabilize any isomer preferentially. The largest differential effect relative to **1**, 9.7 kcal/mol, is found for the μ-hydrido bridged transition structure **7**.

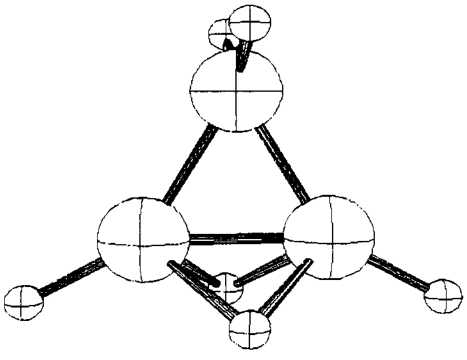
The effect of electron correlation was probed with Møller–Plesset pertubation theory at full fourth order. Significant changes in the relative stability order resulted. Although **1** remains the global minimum at MP4/6-31G*, the relative energies of the other isomers are reduced substantially. Thus, at MP4/6-31G* the Hartree–Fock energy difference between the propylidene dication **3** and **1** is decreased by an impressive 30.2 kcal/mol to only 3.1 kcal/mol! Inclusion of electron correlation at MP2(Full)/6-31G*



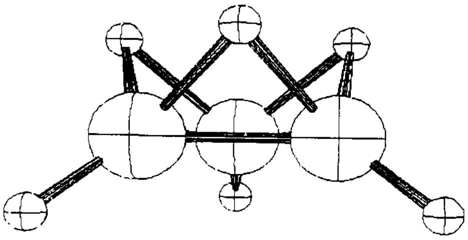
14 C_2



15 C_{2v}



16 C_{2v}



17 C_{3v}

in the geometry optimization gives a very similar energy separation of 3.4 kcal/mol in favor of **1**. However, when zero-point energies are included, isomer **3** becomes slightly more stable (<1 kcal/mol) than dication **1**. Hexacoordinated **10** benefits from a large energy stabilization at MP4 (31.6 kcal/mol), but its energy difference with **1** remains a sizable 53.9 kcal/mol. Comparing the HF and MP4/6-31G* energies, it is evident that those structures containing partial σ or π bonds are stabilized most at correlated levels.

Since both structures **1** and **3** are expected to enjoy significant kinetic stability (see later), their connectivity and H/C-scrambling mechanisms are of interest. Recently related studies were devoted to the ring opening of the cyclopropane radical cation via the trimethylene radical cation to the propylene radical cation. The barrier for terminal H-interconversion in **1** caused by C–C bond rotation (**2**) is 6.5 kcal/mol (0.1 kcal/mol for **3**), while C-scrambling in **1** via **13** requires 39.5 kcal/mol (all MP4/6-31G* + ZPE). The reaction coordinate linking structures **1** and **3**, which would result in the scrambling of all the hydrogens, most likely involves not just a single transition structure (as **14**), but an intermediate like dication **5**. This species, which is 11.8 kcal/mol less stable than **1**, had H-scrambling barriers of 6.1 kcal/mol for the [1,3]-H shift (**7**) and 15.9 kcal/mol (both MP4/6-31G* + ZPE) for the C–C bond rotation (**6**). Structure **5**, in contrast to the trimethylene radical cation, has kinetic stability that may hamper rapid interconversion between **1** and **3**; however, a characterization of such a pathway was not undertaken.

Whereas **1** and **3** may reside in "deep" energy wells on the potential energy surface, the vinyl dication derivatives are local minima of significantly higher energy. Thus, structures **8** and **11** are less stable than **1** by 29.7 and 32.0 kcal/mol (MP4/6-31G* + ZPE), respectively. The pathways linking these vinyl derivatives with **1**, **2**, and **5** have not been established, although [1,2]-H and [1,3]-H shifts seem reasonable. The fascinating hexacoordinated transition structure **10** has the highest relative energy.

Stability toward Dissociation. Owing to the presence of two positive charges, carbodications have an inherent electrostatic driving force favoring dissociation into singly charged units. However, this Coulombic repulsion is countered by the bonding energy even in carbodications as small as the methane dication CH_4^{2+}. This results in kinetically stable species with relatively high barriers;[7a,b,26] the most dramatic example of such behavior is the well-studied He_2^{2+} dication.[27] Moreover, larger dications not only have even higher barriers, but also can be thermodynamically stable toward all possible fragmentations. To assess the stability and to estimate the heats of formation of $C_3H_6^{2+}$ dications, we consider several dissociation modes. These may be evaluated by using the experimental heats of formation for monocations. From our calculated heats of reaction (eq 1-4)[18] and the experimental heats of formation ($\Delta H_f°$ in kcal/mol) of $C_3H_5^+$ (226),[28] $C_3H_3^+$ (256),[28,29] $C_2H_5^+$ (216),[28] $C_2H_3^+$ (267),[28,30] CH_3^+ (261),[28] CH^+ (387),[28] H_3^+ (264),[28] and H^+ (365),[28] an estimated $\Delta H_f°$ of 587 ± 7 kcal/mol is obtained for **1**.

$$C_3H_6^{2+}\ (\mathbf{1}) \rightarrow$$

$$C_3H_5^+ + H^+ \quad +3.8\ \text{kcal/mol (MP3/6-31G*)}\ \{+18.7\ \text{kcal/mol (HF/6-31G*)}\} \quad (1)$$

$$C_3H_3^+ + H_3^+ \quad -58.9\ \text{kcal/mol (MP3/6-31G*)}\ \{-36.5\ \text{kcal/mol (HF/6-31G*)}\} \quad (2)$$

$$C_2H_5^+ + CH^+ \quad +10.7\ \text{kcal/mol (MP4/6-31G*)}\ \{+10.2\ \text{kcal/mol (HF/6-31G*)}\} \quad (3)$$

$$C_2H_3^+ + CH_3^+ \quad -61.0\ \text{kcal/mol (MP4/6-31G*)}\ \{-59.2\ \text{kcal/mol (HF/6-31G*)}\} \quad (4)$$

Using Ibrahim and Schleyer's atom equivalent method,[31] with HF/6-31G* data to estimate heats of formation, $\Delta H_f°$ (**1**) = 564 kcal/mol and $\Delta H_f°$(**3**) = 597 kcal/mol are obtained. Although this method works well for neutral molecules and classical monocations, its reliability has not been widely tested for dications,

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(27) The bonding interactions in He_2^{2+} counter the electrostatic charge–charge repulsions to render a kinetically stable species that has a very short He^+–He^+ bond of 0.741 Å. The barrier for dissociation amounts to 33.2 kcal/mol despite a 200 kcal/mol exothermicity for this process. (a) Pauling, L. *J. Chem. Phys.* **1933**, *1*, 56. (b) Guilhaus, M.; Benton, A. G.; Beynon, J. H.; Rabrenovic', M.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1985**, 210. (c) Guilhaus, M.; Brenton, A. G.; Beynon, J. H.; Rabrenovic', M.; Schleyer, P. v. R. *J. Phys. B* **1984**, *17*, L605.

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(31) Ibrahim, M. R.; Schleyer, P. v. R. *J. Comput. Chem.* **1985**, *6*, 157.

especially where electron correlation effects may be of importance as is the case here.

More accurate heats of formation can usually be deduced from isodesmic reactions, which tend to cancel differences in zero-point and other energies. On the basis of such a reaction (eq 5), using

$$C_3H_6^{2+}\ (\mathbf{1}) + 2CH_4 \rightarrow C_2H_5^+ + CH_3^+ + C_2H_6 \quad -103.8\ \text{kcal/mol (MP4/6-31G*)} \qquad (5)$$

ΔH_f°(exp) $CH_4 = -17.9$ and $C_2H_6 = -20.0$ kcal/mol,[28] $\Delta H_f^\circ(\mathbf{1})$ is estimated to be 596 kcal/mol as an upper limit. Of course, the accuracy of this value depends mainly on the reliability of the theoretical data (e.g., neglect of H-polarization).

The deprotonation of **1** to the allyl cation (and also of **3** to the 2-propenyl cation), reflecting the behavior of isolated species (eq 1), is endothermic, but only by 3.8 kcal/mol at MP3/6-31G*. However, significant barriers are observed for deprotonation in the absence of solvation, i.e., in the gas phase. While determination of a transition structure for this process was beyond our scope, the data on other dications is informative. For example, small dications (with calculated deprotonation energies and associated barriers given in kcal/mol) like CH_4^{2+} (106, 16.8),[7a] CH_6^{2+} (63, 35.4),[7b] $C_2H_2^{2+}$ (10, 65),[7d] and $C_2H_4^{2+}$ (16, 65)[7e] show that even very exothermic deprotonations have substantial barriers.

Although the demethylation of **1** (eq 4) is exothermic by −61.0 kcal/mol, structure **1** is not a credible candidate for such a process because it does not possess a methyl group. Instead, **3** and possibly **5** would be more likely candidates for such a disproportionation. However, demethylation of **3** would require a significant structural reorganization to yield a stable $C_2H_3^+$ fragment (other than CH_3–C^+). Henceforth, we predict both structures **1** and **3** to be viable species for mass spectrometric observation, possibly from charge-stripping experiments on propene and cyclopropane. The corresponding radical cations have already been studied experimentally and theoretically.[9] Whereas isomer **11** may fragment to the cyclopropenium ion and H_3^+ (compare eq 2), dissociation of **8** is more likely to produce the isomeric propargyl cation and H_3^+. Although these processes are exothermic by 95 and 61 kcal/mol, respectively, sizable barriers are expected on basis of the required structural deformations. For example, the 127 kcal/mol exothermic dissociation of CH_6^{2+} to $CH_3^+ + H_3^+$ has an activation barrier of 59.9 kcal/mol.[7b] Charge-separation experiments could provide additional information about fragmentation modes. However, March's proposal[8a] for a cyclic structure, based on the intercharge distance of 2.36 Å for the charge separation, deduced for the 6.1-eV kinetic energy release for deprotonation, does not seem very likely.

Ionization Energies. Calculated adiabatic dioxidation from neutral precursors can be related to the corresponding appearance potentials that may be obtained in charge-exchange reactions. The estimated energy required to form **5** directly from propylene is 25.4 eV, whereas the energy difference between propylene and dication **3** is 25.0 eV (both at MP4/6-31G*).[32b] If adiabatic dioxidation of cyclopropane[32b] directly affords dication **1**, a minimal energy of 24.6 eV is required for this process; the energy difference between cyclopropane and **13** is 26.3 eV (also MP4/6-31G*). No experimental data are currently available.

Using the isogyric reaction (eq 6),[32] which partly avoids the

$$C_3H_6^{2+} + e + H_2 \rightarrow C_3H_6^{\bullet+} + 2H^\bullet \qquad (6)$$

difficulties associated with accurate computation of the correlation energy between paired electrons, employing MP2/6-31G* data[33] and the $D_e(H_2)$ of 0.17447 hartree gives an adiabatic ionization energy $IE_a(R^{\bullet+}$–$R^{2+})$ of 15.9 eV for **1** from the cyclopropane radical cation and an IE_a of 16.9 eV for the generation of **5** from the propene cation radical; adiabatic oxidation of the latter to dication **3** would require 16.5 eV.[32a] These values may be compared with the experimental Q_{min} values that are obtained from charge-stripping experiments on the corresponding radical cations. However, the observed value[8b] of 18.2 eV seems out of range and may reflect a vertical process or ionization to an excited dication.

Conclusions

The important points from the present study can be summarized as follows.

1. The protonated allyl cation (**1**) and the propylidene dication (**3**) have nearly the same energy and are the two most stable $C_3H_6^{2+}$ isomers. Both are predicted to be observable in the gas phase.

2. Bishyperconjugation, which is the combined hyperconjugative effect on the same C–H bond(s) by two adjacent centers, stabilizes the protonated allyl cation, while the propylidene dication benefits from crosshyperconjugation, which is the hyperconjugation effect in two orthogonal planes.

3. The propylene dication **5** is 12.6 kcal/mol less stable than the propylidene dication **3** at MP4/6-31G* + scaled ZPE.

4. Dioxidized planar cyclopropane **13** is not a minimum on the $C_3H_6^{2+}$ potential energy surface.

5. The energy orderings of the $C_3H_6^{2+}$ dications is very different from those reported for the $C_3H_6^{\bullet+}$ radical cations, where the propene isomer is more stable than the cyclopropane isomer, both favored energetically over the trimethylene radical cation.

6. The barrier for the [1,3]-H sigmatropic shifts in the propylene dication is 6.2 kcal/mol.

7. The [1,2]-CH_4 sigmatropic shift in the vinyl-substituted methonium ion CH_4–CH–CH^{2+} has a transition structure with a hexacoordinated carbon. The barrier for this process is 21.9 kcal/mol.

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