Gitonic and Distonic Alkanonium Dications (Diprotonated Alkane Dications $C_nH_{2n+4}{}^{2+}$, $n = 1-4$)[1]

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The structures and stabilities of gitonic and distonic alkanonium dications, i.e., diprotonated alkane dications $C_nH_{2n+4}{}^{2+}$ ($n = 1-4$), were investigated at the MP4(SDTQ)/6-311G**//MP2/6-31G** level. The global minimum energy structures (**2**, **4**, **7**, and **10**) of the $C_nH_{2n+4}{}^{2+}$ dications are double C−H protonated alkanes to give structures with two two electron three-center (2e-3c) bonds. Two different dissociation pathways for the dications, viz deprotonation and demethylation, were also computed. Demethylation was found to be the favorable mode of dissociation.

Introduction

Since the discovery of triphenylmethyl cations 100 years ago,[2] the field of carbocations has grown into maturity. Stereochemical and kinetic studies of acid-catalyzed processes led to their indirect identification in the 1940s and 1950s.[3] Olah's development of superacidic stable ion conditions in the early 1960s enabled their direct study. Since that time, a great variety of diverse carbocations (both carbenium and carbonium ion type) have been investigated by spectroscopic means (NMR, IR, UV−vis, ESCA, X-ray), theoretical calculations, and chemical studies.[4] Carbodications are also of increasing significance both in solution and in gas-phase chemistry. Their structural properties have been addressed in several reviews.[5] The majority of the studied long-lived carbodications involve trivalent sp^2-type carbenium ion centers separated by two or more carbon atoms.[5e] Diprotonated methane, $CH_6{}^{2+}$, is the parent six-coordinate carbodication. Its structure was calculated by Lammertsma et al. at the ab initio HF/6-31G* level.[6]

Kekule's[7] four-valent classical bond theory is unable to explain bonding in higher coordinate carbocations.

$CH_5{}^+$ $CH_6{}^{2+}$ $CH_7{}^{3+}$

$C_2H_8{}^{2+}$
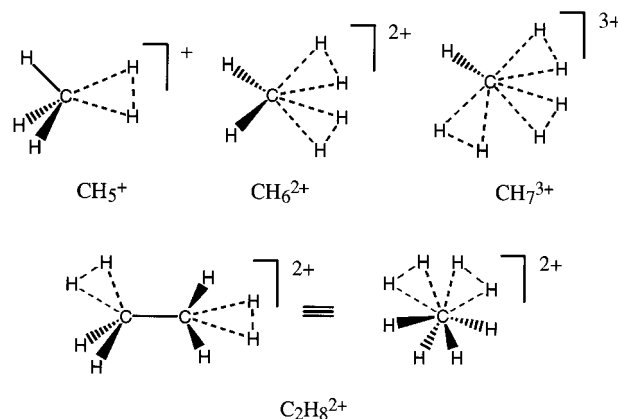
These require the involvement of two-electron three-center (2e-3c) bonds as suggested by Olah.[8] Such bonding is key to the σ-bond reactivity of saturated hydrocarbons in strong acids. The ultimate example is the global energy minimum structure of the $CH_6{}^{2+}$ dication, which contains two 2e−3c (carbonium-type) bonds.[6]

The parent five-coordinate carbonium ion is $CH_5{}^+$. High-level ab initio studies reconfirmed[9] the preferred global minimum C_s symmetrical structure[10] with a 2e-3c bond as suggested originally by Olah.[11] The assumed ready bond-to-bond (polytopal) rearrangements were later confirmed by Schleyer et al.,[10a] who showed $CH_5{}^+$ to be a highly fluxional, completely delocalized structure by high-level calculations. Subsequently, we have reported that even the parent seven-coordinate carbotrication, triprotonated methane ($CH_7{}^{3+}$), is an energy minimum with three 2e-3c bonding interactions.[12]

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Table 1. Total Energies (−au), ZPE,[a] and Relative Energies (kcal/mol)[b]

	MP2/6-31G**// MP2/6-31G**	ZPE	MP4(SDTQ)/ 6-311G**// MP2/6-31G**	rel energy (kcal/mol)
CH_6^{2+} **1**	40.47806	35.1	40.52061	0.0
CH_6^{2+} **1a**	40.47195	33.5	40.51548	1.6
$C_2H_8^{2+}$ **2**	79.77248	53.7	79.84502	0.0
$C_2H_8^{2+}$ **3**	79.77205	53.9	79.84471	0.4
$C_3H_{10}^{2+}$ **4**	119.01121	72.4	119.11435	0.0
$C_3H_{10}^{2+}$ **5**	118.97373	71.8	119.07733	22.6
$C_3H_{10}^{2+}$ **6**	118.99611	72.2	119.10299	6.9
$C_4H_{12}^{2+}$ **7**	158.20426	89.6	158.33817	0.0
$C_4H_{12}^{2+}$ **8**	158.17491	89.3	158.30953	17.7
$C_4H_{12}^{2+}$ **9**	158.19651	89.3	158.33363	2.6
$C_4H_{12}^{2+}$ **10**	158.22800	90.1	158.36156	0.0
$C_4H_{12}^{2+}$ **11**	158.22504	91.1	158.36104	1.3

[a] Zero point vibrational energies (ZPE) at MP2/6-31G**//MP2/6-31G** scaled by a factor of 0.96. [b] At MP4(SDTQ)/6-311G**//MP2/6-31G** + ZPE level.

Diprotonated ethane ($C_2H_8^{2+}$) was studied[6a] by Lammertsma et al. The HF/6-31G* calculated structure (C_2 symmetry) contains two pentacoordinated carbons with a 2e-3c bonding interactions on each. This again demonstrates the general importance of 2e-3c interactions in protonated alkanes. Formation of di- and polycations in superacid solutions was recognized by Olah to involve not only saturated hydrocarbons but also many Lewis bases containing nonbonded electron pair donors.[13] Such protonation or protosolvation in the limiting case can lead to gitonic (in which the positive charge bearing centers can be adjacent or geminal) or distonic (in which the positive charge bearing centers are separated by at least one carbon) onium dications. We herein report ab initio calculations to establish the structures and relative stabilities of the diprotonated gitonic and distonic alkane dications $C_nH_{2n+4}^{2+}$ ($n = 1-4$).

Calculations

The Gaussian 98 program was used for all calculations.[14] Geometries were optimized at the ab initio MP2/6-31G** level.[15] Vibrational frequencies at the MP2/6-31G**//MP2/6-31G** level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) and to evaluate zero-point vibrational energies (ZPE), which were scaled by a factor of 0.96.[16] For improved energies single-point MP4(SDTQ)/6-311G** calculations were performed on MP2/6-31G** optimized geometries and ZPE energies were taken into account. All energies are given in Table 1. MP2/6-31G** geometrical parameters and final energies will be discussed throughout, unless stated otherwise.

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Results and Discussion

CH_6^{2+}. The structure of gitonic CH_6^{2+} dication was previously calculated (at the HF/6-31G* level) by Lammertsma et al.[6] We have recalculated CH_6^{2+} only to compare it with other alkane dications. The calculated C_{2v} symmetric stable minimum **1** for CH_6^{2+} dication with two 2e-3c bonds is shown in Figure 1. The CH_6^{2+} dication has not yet been observed experimentally. However, the isoelectronic boron analogue BH_6^+, which was also found to be a C_{2v} symmetrical with two 2e-3c bonds,[17,18] has recently been observed in the gas phase by DePuy et al.[17]

The transition structure, **1a** (Figure 1), for intramolecular hydrogen transfer has an energy difference of only 1.6 kcal/mol with the CH_6^{2+} structure **1**. This shows that hydrogen scambling in the dication has a modest barrier. However, in the parent five-coordinated carbocation CH_5^+, such a barrier for the scrambling of its five hydrogens becomes extremely small (few calories/mol),[9] the completely delocalized 6c-8e structure as suggested by Schlyer et al.[10a] is not the lowest energy minimum for CH_5^+. The barrier for deprotonation in **1** was also calculated and found to be 38.7 kcal/mol.

$C_2H_8^{2+}$. Lammertsma et al. also calculated[6a] the $C_2H_8^{2+}$ dication at the HF/6-31G* level and found the C_2 symmetrical structure **3** as the only minimum. However, our present calculations at the MP2/6-31G** level show that both C_2-symmetrical **3** and C_{2h} structure **2** (Figure 1) are the minima on the potential energy surface (PES). In fact, **2** is with 0.4 kcal/mol slightly more stable than **3** (Table 1). The two 2e-3c units of **3** are almost perpendicular to each other, while they have an anti orientation in **2**. No transition structure for the deprotonation in the dication **2** could be located.

$C_3H_{10}^{2+}$. Structures **4**−**6** were located as minima on the PES of diprotonated propane $C_3H_{10}^{2+}$ (Figure 1). In the C_{2v} symmetrical structure **4**, both terminal carbons contain electron-deficient 2e-3c bonds while in structure **5** this is the case for one terminal and the central carbon. Structure **6** can be viewed as a C−H and C−C bond diprotonated propane. Structure **4** is substantially more stable than **5** by 22.6 kcal/mol (Table 1). This is expected because in the *gitonic* dication **5** the formally positive charge bearing centers are adjacent whereas in *distonic* dication **4** they are separated by one carbon. The structure **4** is also more stable than **6** by 6.9 kcal/mol.

$C_4H_{12}^{2+}$. Similar to diprotonated propane, three analogous structures (**7**−**9**) were found to be as stable minima for diprotonated isobutane $C_4H_{12}^{2+}$ (Figure 1). Distonic dication **7** is 17.7 kcal/mol more stable than the gitonic dication **8** (Table 1). Again, charge−charge repulsion is the primary reason for this substantial energy difference. However, the C−H, C−C diprotonated form **9** is only 2.6 kcal/mol less stable than **7**.

Structures of diprotonated *n*-butane dications were also investigated. The only terminal C−H diprotonated form **10** and the terminal C−H and C−C diprotonated form **11** were found to be minima. Structure **10** is slightly more stable than **11** by 1.3 kcal/mol.

Two different dissociation paths for the larger dications, deprotonation (eq 1) and demethylation (eq 2), were

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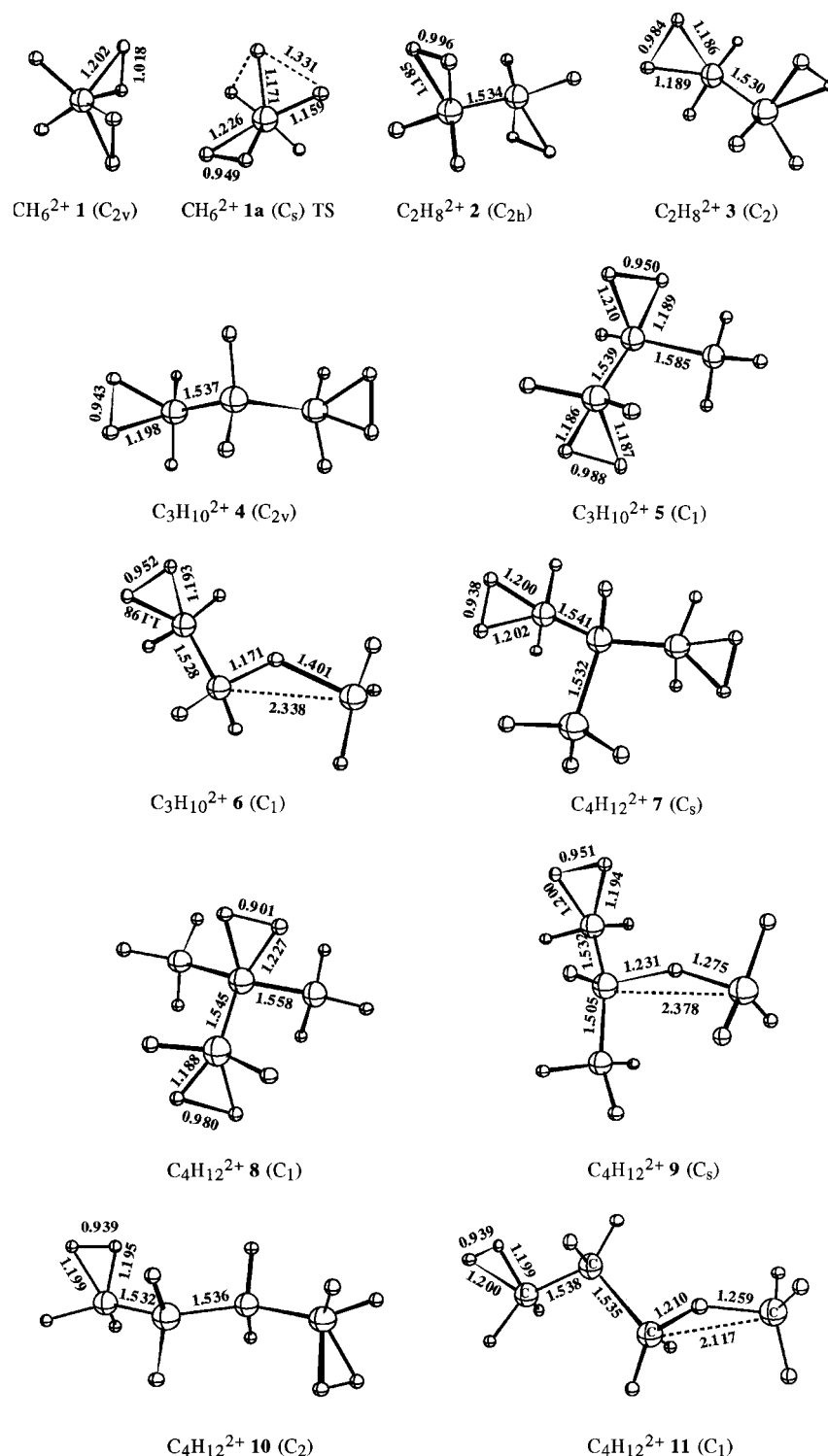
Figure 1. MP2/6-31G** structures of **1**−**11**.

considered. In harmony with literature data, the deprotonation of diprotonated methane **1** is, as anticipated, highly exothermic with 63.2 kcal/mol. In contrast, and has been noted before, the deprotonation energy of diprotonated ethane **2** is with 1.2 kcal/mol slightly endothermic. The deprotonation energies of **4** (to give 2-protonated propane), **7** (to give 2-protonated isobutane), and **10** (to give 2-protonated *n*-butane) are rather strongly endothermic by 30.7, 31.2, and 50.3 kcal/mol, respectively (Table 2). Structure of 2-protonated propane and 2-pro-

tonated isobutane were recently calculated by Mota et al.[19] and Sommer et al.[20] by ab initio methods.

Compared to the deprotonations, the demethylations (loss of CH_3^+) are thermodynamically much more favorable. Thus, dissociations of **2** into CH_5^+ and CH_3^+, of **4** into $C_2H_7^+$ and CH_3^+, of **7** into $C_3H_8^+$ and CH_3^+, and of

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Table 2. Calculated ΔH of Selected Processes[a]

process	ΔH (kcal/mol)
CH_6^{2+} **1** $\rightarrow$ CH_5^+ + H^+	−63.2
$C_2H_8^{2+}$ **2** $\rightarrow$ $C_2H_7^+$ + H^+	+1.2
$C_2H_8^{2+}$ **2** $\rightarrow$ CH_5^+ + CH_3^+	−96.7
$C_3H_{10}^{2+}$ **4** $\rightarrow$ $C_3H_9^+$ + H^+	+30.7
$C_3H_{10}^{2+}$ **4** $\rightarrow$ $C_2H_7^+$ + CH_3^+	−67.0
$C_4H_{12}^{2+}$ **7** $\rightarrow$ $C_4H_{11}^+$ + H^+	+31.2
$C_4H_{12}^{2+}$ **7** $\rightarrow$ $C_3H_9^+$ + CH_3^+	−64.6
$C_4H_{12}^{2+}$ **10** $\rightarrow$ $C_4H_{11}^+$ + H^+	+50.3
$C_4H_{12}^{2+}$ **10** $\rightarrow$ $C_3H_9^+$ + CH_3^+	−50.4

[a] At MP4(SDTQ)/6-311G**//MP2/6-31G** + ZPE level.
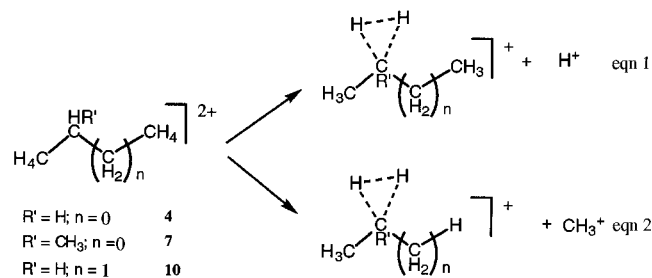
10 into $C_3H_8^+$ and CH_3^+ are exothermic by 96.7, 67.0, 64.6, and 50.4 kcal/mol, respectively.

Acid-catalyzed hydrocarbon transformations are important industrial processes. The ability of strong superacids to further protosolvate[13] (protonate) alkane cations might have significant implications in hydrocarbon transformations. Although such reactive alkane dications are not observed by slow spectroscopic methods (such as NMR) as persistent species in superacid media, computational characterization gives additional support for their transient existence and involvement in superacid catalyzed processes. Recently, we have been able to show by hydrogen/deuterium exchange experiments and by theoretical calculations that long-lived stable alkyl cations, such as *tert*-butyl and 2-propyl cations, undergo C−H protonation in superacids to form highly electron deficient protioalkyl dications (gitonic carbenium-car-

bonium dications).[21] In the condensed phase, electrophilic (protolytic) solvation or clustering effects may have great influence on dications. In particular, in small dications, such interactions should diminish the effect of charge−charge repulsion and thus could bring the cations into more thermodynamically feasible range.[13]

R = H   protio 2-propyl dication
R = CH₃   protio *tert*-butyl dication
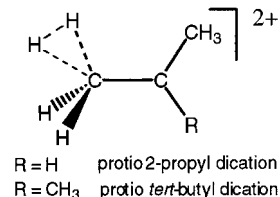
As shown in previous studies, distonic carbenium dications are observable in superacidic media, generally when the two carbocationic centers are separated by two carbon atoms (1,4-dications), while some examples of 1,3-dications and recently some gitonic 1,2- and 1,1-dications ($CH_2^+CH_2^+$ and CH_2^{2+}) have so far been studied only computationally.

Conclusion

This ab initio study at the MP2/6-31G** level shows that the global minima of the $C_nH_{2n+4}^{2+}$ ($n = 1-4$) dications are double C−H protonated alkanes resulting in structures with two 2e-3c bonds, i.e., **2**, **4**, **7**, and **10**. The C−H and C−C diprotonated propane **6**, isobutane dication **9** and *n*-butane dication **11** were also found to be the minima but they are less stable than their corresponding double C−H protonated analogues **4**, **7** and **10**, respectively. Of the two different dissociation paths for the dications, demethylation was found to be significantly more favorable than deprotonation.

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