Ab Initio Study of the Structures and Stabilities of the Dimer of Ethyl Cation, $(C_2H_5^+)_2$ and Related $C_4H_{10}^{2+}$ Isomers[1]

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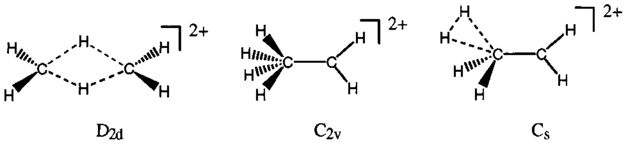
Ab initio calculations at the MP4(SDTQ)/6-311G**//MP2/6-31G** level were performed to study the structures and stabilities of the dimer of ethyl cation, $(C_2H_5^+)_2$, and related $C_4H_{10}^{2+}$ isomers. Two doubly hydrogen bridged diborane type trans **1** and cis **2** isomers were located as minima. The trans isomer was found to be more favorable than cis isomer by only 0.6 kcal/mol. Several other minima for $C_4H_{10}^{2+}$ were also located. However, the global energy minimum corresponds to C−H (C_4 position) protonated 2-butyl cation **10**. Structure **10** was computed to be substantially more stable than **1** by 31.7 kcal/mol. The structure **10** was found to be lower in energy than 2-butyl cation **13** by 34.4 kcal/mol.

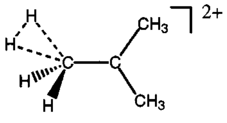
Introduction

The dimer of methyl cation ($C_2H_6^{2+}$) was first investigated theoretically by Olah and Simonetta[2] who found that a doubly bridged, diborane like D_{2d} symmetric structure (Chart 1) is a minimum. Later Schleyer and Pople[3] showed that the C_{2v} symmetrical carbenium−carbonium ion isomer is energetically favored over the diborane-like structure by 9.0 kcal/mol at the MP4SDQ/6-31G**//HF/6-31G* level. Subsequently, Olah et al.[4] showed that the global minimum of this dication is a C_s symmetrical structure with a three center, two electron (3c−2e) bond. This carbenium−carbonium dication structure can be considered either as a complex between H_2 and the ethylene dication, $C_2H_4^{2+}$, or as the protonated ethyl dication. The C_s symmetrical structure is 3.5 kcal/mol more stable than the C_{2v} symmetrical structure. The $C_2H_6^{2+}$ dication has also been observed experimentally by charge stripping of $C_2H_6^{+\cdot}$ radical cation in a mass spectrometer.[5]

No study of the dimer of ethyl cation, however, has been reported. Whereas destabilization by Coulomb repulsion cannot be alleviated through substituent effect in dimer of methyl cation, it should be possible to stabilize by introducing methyl substituents. In fact recently we have been able to show by hydrogen/deuterium exchange experiments and by theoretical calculations that long-lived stable *tert*-butyl[6] as well as isopropyl[7] cations undergo C−H protonation in superacids to form highly electron deficient protio *tert*-butyl and protio isopropyl dications, respectively (gitonic carbenium−carbonium dications).

Chart 1





protio *tert*-butyl dication

We herein report ab initio calculations to establish the structures and stabilities of the dimer of ethyl cation, $(C_2H_5^+)_2$, and related $C_4H_{10}^{2+}$ isomers.

Calculations

All calculations were carried out with the Gaussian 98 program.[8] The geometry optimizations were performed at the MP2/6-31G** level.[9] 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)

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

no.	MP2/6-31G**//MP2/6-31 G**	ZPE	NIMAG[c]	MP4(SDTQ)/6-311G**//MP2/6-31G**	rel. energy (kcal/mol)
1	156.983 24	77.1	0	157.110 54	31.7
2	156.982 64	77.1	0	157.109 70	32.3
3	156.994 57	75.1	0	157.122 01	26.5
4	156.990 25	79.7	0	157.118 67	24.0
5	157.001 38	78.1	0	157.124 54	22.0
6	157.029 95	78.1	0	157.151 76	4.9
7	156.990 15	77.9	0	157.112 20	29.9
8	156.964 49	77.3	0	157.088 26	45.5
9	156.963 66	77.2	0	157.087 42	46.1
10	157.038 43	75.9	0	157.163 02	0.0
10ts	156.897 96	72.0	1	157.021 65	84.8
11	157.030 67	76.6	0	157.155 14	4.2
12	157.020 64	75.3	0	157.145 62	11.5
13	156.999 041	73.0	0	157.112 81	34.4
14	78.591 27	38.0	0	78.653 30	

[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. [c] Number of imaginary frequency (NIMAG).

which were scaled by a factor of 0.96.[10] For improved energy, single point energies at MP4(SDTQ)/6-311G** on MP2/6-31G** optimized geometries were computed. Final energies were calculated at the MP4(SDTQ)/6-311G**//MP2/6-31G** + ZPE level. Calculated energies are given in Table 1.

Results and Discussion

Doubly hydrogen bridged trans **1** and cis **2** isomers of ethyl cation dimer ($C_4H_{10}^{2+}$) were located as minima (Figure 1). The two ethyl cations in **1** and **2** are bonded by a four center, two electron (4c−2e) bond resulting in gitonic (in which the positive charge bearing centers can be adjacent or geminal) carbonium dication. The trans isomer was found to be only 0.6 kcal/mol more stable than the cis isomer. The calculated central and terminal C−C and the bridged C−H bond lengths of **1** are 1.627, 1.471, and 1.268 Å, respectively. Dissociation of the trans dication into two ethyl cations ($C_2H_5^+$) was computed to be exothermic by 121.9 kcal/mol. A hydrogen bridged diborane-like structure was also calculated for dimer of methyl cation $C_2H_6^{2+}$.[2] We have also calculated *gem*-dimethyl substituted structure **3**. The C_{2v} structure **3** was found to be 5.2 kcal/mol more stable than **1** (Table 1). The structure **3** can be considered as a complex between $(CH_3)_2C^{2+}$ dication and neutral CH_4. However, the inetraction of the methane C−H bonds with the carbocationic center is probably very weak as indicated from the very long bridged C−H bond lengths of 1.524 Å and the long C−C bond length of 1.676 Å. The structure **3** was reported before by Olah et al.[6]

The minimum structure **4** (C_{2h} symmetry), also doubly hydrogen bridged, can be considered as head to tail complex of two ethyl cations (Figure 1). The six-member ring structure adopt a chair conformation. The calculated C−C and the bridged C−H bond lengths of the structure are 1.522 and 1.248 Å, respectively. This was found to be 7.7 kcal/mol more stable than **1**.

We have also located several other minima on the potential energy surface of $C_4H_{10}^{2+}$. Structure **5** (Figure 1) corresponds to a doubly edge-protonated methyl cyclopropane, in analogy to the previously identified *arachno*-$Me_2CBH_4^+$ cation (a complex between 2-propyl cation and borane).[11] This can be considered as either a complex between ethane and ethylene dication or a complex between 1,1-diprotonated acetylene dication and ethane. The species **5** was computed to be 9.7 kcal/mol more stable than **1**.

Structure **6** can be viewed as edge and methyl C−H diprotonated methyl cyclopropane. On the other hand, **7** can be considered as edge and methine C−H diprotonated methylcyclopropane. Both were found to be as energy minima. Structure **6** is substantially more stable than **7** by 25.0 kcal/mol (Table 1). This is because in the dication **7** the positive charge bearing centers are adjacent (gitonic), whereas in dication **6** they are separated by one carbon (distonic). Structure **6** is also more stable than **1** by 26.8 kcal/mol.

Minimum structure **8** with two 3c−2e bonds can be considered as diprotonated cyclobutane dication. Two C−C bonds (1.592 and 1.589 Å) of the cyclobutyl ring are substantially longer than the remaining C−C bonds (1.551 and 1.543 Å). This is because the electron deficient 3c−2e bond is almost perplanar with the long bond resulting in more hyperconjugative interaction. On the other hand, it is perpendicular with the short bond resulting in less interaction. The two 3c−2e units of **8** are in trans orientation. The structure **9** with cis orientation of two 3c−2e units also corresponds to a stable minimum. Energetically, **8** and **9** are almost identical. However, they are significantly less stable than **1** (by about 14 kcal/mol).

Global energy minimum for $C_4H_{10}^{2+}$ was found to be C_s symmetrical structure **10**. The structure corresponds to a C−H (C_4 position) protonated 2-butyl cation. The structure contains a carbonium ion center involving a 3c−2e bond and a trivalent sp^2-type carbenium ion center separated by a carbon atom. This carbenium−carbonium structure **10** is substantially more stable than **1** by 31.7 kcal/mol (Table 1). This is because in the *gitonic* dication **1** the formally positive charge bearing centers are adjacent, whereas in *distonic* dication **10** they are separated by one carbon. Interestingly, the structure **10** was found to be lower in energy than 2-butyl cation by 34.4 kcal/mol. Thus, the protonated 2-butyl cation **10** is thermodynamically more favorable than 2-butyl cation when considered as isolated species in the idealized gas phase. In dications, such as **10** despite charge−charge repulsion there is remarkable bonding interaction. This shows that similar to *tert*-butyl cation,[6] 2-butyl cation probably could undergo proton−deuterium exchange

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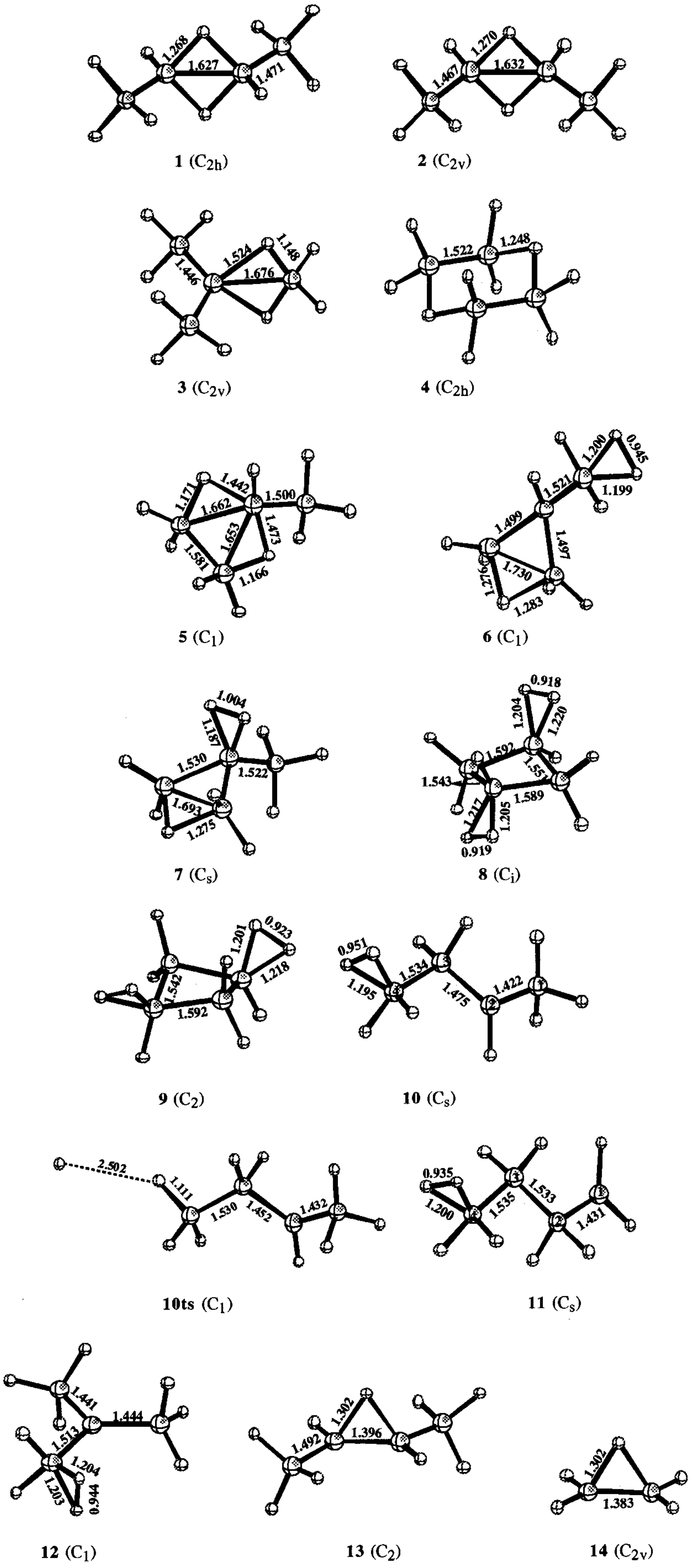


1 (C_{2h}) **2** (C_{2v})

3 (C_{2v}) **4** (C_{2h})

5 (C_1) **6** (C_1)

7 (C_s) **8** (C_i)

9 (C_2) **10** (C_s)

10ts (C_1) **11** (C_s)

12 (C_1) **13** (C_2) **14** (C_{2v})

Figure 1. MP2/6-31G** optimized structures of **1**−**14**.

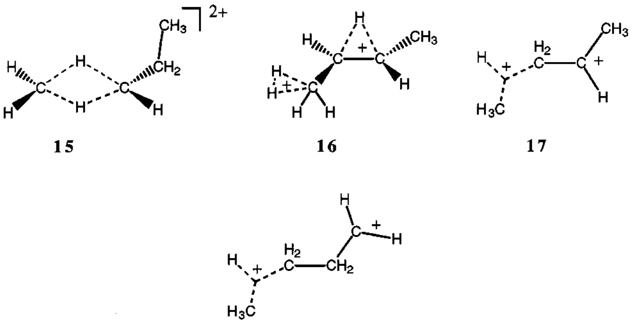
under superacidic conditions. The C1−C2 bond (1.422 Å) of **10** is considerably shorter than C2−C3 bond (1.475 Å). These data suggest that hyperconjugative stabilization of the carbenium ion center involving CH_2 (C3) group is partly diminished by protonation on CH_3 (C4) group. No significant methyl-H bridging between the carbenium ion center and CH_3 (C1) group was observed in dication **10**.

Two different dissociation paths for the global minimum structure **10**, namely deprotonation and demethylation, were considered. Whereas the deprotonation of **10** is endothermic by 34.4 kcal/mol, demethylation is exothermic by 66.0 kcal/mol. We have identified the transition structure **10ts** (Figure 1) for deprotonation of **10**, which lies 84.8 kcal/mol above **10** (Table 1). Thus, dication **10** has a very high kinetic barrier for deprotonation. However, no transition structure for demethylation of **10** could be located. Dissociation of **10** into two ethyl cations is even more exothermic by 90.2 kcal/mol.

The possible structure **11** corresponding to a C−H (C_4 position) protonated 1-butyl cation was also calculated. Unlike **10**, in *distonic* dication **11** the formally positive charge bearing carbenium and carbonium centers are separated by two carbons. Despite this **11** is 4.2 kcal/mol less stable than **10**. This is because the dication **11** contains a unfavorable primary carbenium ion unit. It was also found that structure **11** (without any symmetry constrain) do not covert into structure **10** upon optimization. On the other hand, the carbenium carbonium structure **12** corresponds to a C−H protonated *tert*-butyl cation. Structure **12** was previously calculated by Olah et al.[6] As we mentioned above long-lived stable *tert*-butyl cation were found to undergo upon addition of deuterated superacid isotopic hydrogen/deuterium exchange involving protonated *tert*-butyl cation **12**.[6] Structure **12** was found to be 20.2 kcal/mol more stable than **1** but 11.5 kcal/mol less stable than **10**. Structures of **10**−**12** together with 2-butyl cation **13** and ethyl cation **14** are depicted in Figure 1. Attempts to find stable minima for possible structures **15**−**18** (Chart 2), however, failed because of rearrangement to form the more stable structures **6**, **10**, and **11** (Figure 1), respectively.

Alkyl cations such as 2-butyl cation are stabilized not only by weak external solvation but also intramoleculary by C−C or C−H hyperconjugation. These hyperconjugative interactions with the carbocationic center contribute to the overall stability of the ion. The more stable an alkyl cation, the lower its reactivity. On the other hand, with further protonation of alkyl cation in superacidic solutions such as the protio 2-butyl dication **10** C−H hyperconjugative stabilization would be decreased. This would lead to an enhanced electron deficiency and reactivity of the carbocationic center. This type of protosolvation[12] (protonation) of alkyl cations might also have significant implications in hydrocarbon transformations catalyzed by strong acids. As our previous studies have demonstrated *tert*-butyl[6] and even 2-propyl[7] cations can be activated protolytically in superacid solutions. In the limiting case protolytic interaction of alkyl cations in superacids can de facto result in formation of protioalkyl dications, as demonstrated by isotopic hydrogen−deuterium exchange studies and theoretical calculations. It is now suggested that the superacidic protonation of 2-butyl dication might be a suitable way to generate dication **10**.

Chart 2



15 **16** **17** **18**

Conclusion

Structures of the dimer of ethyl cation, $(C_2H_5^+)_2$, and related $C_4H_{10}^{2+}$ isomers were calculated at the ab initio MP2/6-31G** level. Doubly hydrogen bridged trans **1** and cis **2** isomers were located as minima with the trans isomer being only 0.6 kcal/mol more stable than the cis isomer. Several other minima on the potential energy surface of $C_4H_{10}^{2+}$ were located. Global energy minimum was found to be C−H (C_4 position) protonated 2-butyl cation **10**. The carbonium−carbenium dication **10** was computed to be substantially more stable than **1** by 31.7 kcal/mol. The structure **10** was found to be lower in energy than 2-butyl cation **13** by 34.4 kcal/mol.

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Supporting Information Available: Cartesian coordinates and total energies (hartrees) of the optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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