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Superelectrophilic Protio Methyl- and Protio Dimethylmethyleniminium Dications[1]

George. A. Olah,* G. K. Surya Prakash, and Golam Rasul

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661

olah@usc.edu

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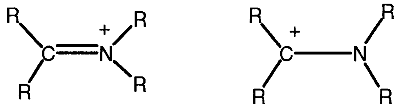
Electronic structures and energies of superelectrophilic dications derived by protonation of methyl- and dimethylmethyleniminium ($R'R''C{=}N^+R'R''$; R', $R'' = CH_3$ or H) ions were calculated at the ab initio MP2/6-311+G** level. The calculations identified the N-protonated isopropyleniminium dication **14** as a minimum structure. On the basis of computed energies, deprotonation energies of the global minimum structures were also calculated. The ^{13}C NMR chemical shifts of the intriguing dication **14** were calculated using the GIAO-MP2 method. The ^{13}C NMR chemical shifts of the isoelectronic analogue *tert*-butyl cation were also calculated at the same level in order to explore the effect of an additional charge in dications **14**.

Introduction

In 1978, Olah and Donovan reported[2] preparation and study of methyleniminium ($CH_2{=}NH_2^+$) and a number of methylmethyleniminium ions. From a ^{13}C NMR spectroscopic and theoretical CNDO/2 study it has been shown that these ions are predominantly iminium ions **I** with limited contribution from aminocarbenium ion structures **II** (Scheme 1). This is due to the ability of the nonbonded electron pair of the nitrogen atoms to stabilize the adjacent positive charge. The C methyl substituents slightly change the importance of **I** relative to **II**, but **I** still remains the dominant contributor to the overall structure. The iminium ions are by nature ambident carbocationic and therefore should be able to act as electrophilic aminoalkylating agents. However, if the nonbonded electron pairs of the nitrogen atom of these ions were affected by further protolytic (or electrophilic) interaction, the electron deficiency of the corresponding carbocationic centers would become more pronounced, resulting in enhanced superelectrophilic reactivity.[3]

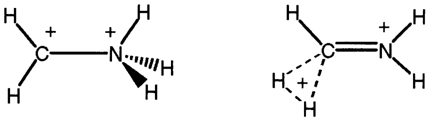
We recently reported[4] the calculated structures of protonated methyleniminium cations by using ab initio methods. Both C and N (Scheme 2) protonated methyleniminium dications, **III** and **IV**, respectively, are minima on the potential energy surface (PES). The NH_3-substituted methyl cation **III** is 27.6 kcal/mol more stable than the three-center two-electron (3c−2e) bonded structure **IV**. Schwarz et al. investigated[5] the ethylamine radical cation ($CH_3NH_2^{+\bullet}$) ion by charge stripping mass spectrometry. Charge stripping resulted in the formation of the dication **III**.

SCHEME 1



I **II**

SCHEME 2



III **IV**

The important role of protosolvation of nonbonded electron pairs, π-electrons, and even σ-electrons of carbocations and onium ions in superacid solutions is by now well-recognized.[3] Such protosolvation in the limiting case can lead to gitonic dications in which the positive charge bearing centers can be adjacent.[3] In continuation of our studies, we now report ab initio studies to investigate the electronic structure and properties of protonated methyl- and dimethylmethyleniminium dications. The present study adds further to our understanding of the role of protosolvation in superacid chemistry.

Calculations

Calculations were carried out with the Gaussian 98 program.[6] The geometry optimizations were performed at the MP2/6-31G** level. 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)] or transition state (NIMAG = 1) and to evaluate zero-point vibrational energies (ZPE), which were scaled by a factor

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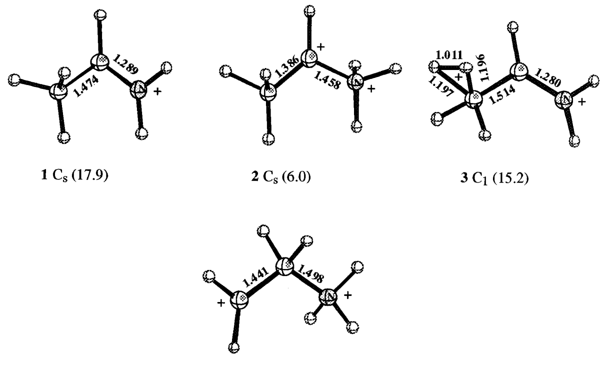
TABLE 1. Total Energies (−au) Calculated at Different Levels, ZPE,[a] and Relative Energies (kcal/mol)[b]

no.	MP2/6-31G**//MP2/6-31G**	ZPE	MP2/6-311+G**//MP2/6-311+G**	MP4(SDTQ)/6-311+G**//MP2/6-311+G**	rel energy (kcal/mol)
1	133.896 99	51.0	133.941 16	133.993 14	17.9
2	133.920 05	55.0	133.964 17	134.018 51	6.0
3	133.904 71	54.4	133.949 82	134.002 88	15.2
4	133.933 61	56.9	133.975 88	134.031 11	0.0
5	133.880 88	51.2	133.924 58	133.977 74	0.0
6	133.825 76	53.2	133.871 29	133.925 95	34.5
7	133.873 92	54.8	133.919 50	133.973 71	6.1
8	173.083 62	68.5	173.140 40	173.210 99	24.2
9	173.129 12	74.2	173.186 08	173.258 58	0.0
10	173.049 68	70.5	173.109 18	173.181 34	44.8
11	173.094 16	71.8	173.153 23	173.224 91	18.7
12	173.106 20	71.7	173.164 29	173.235 85	11.8
13	173.098 92	68.3	173.156 24	173.225 66	31.3
14	173.152 59	72.5	173.210 26	173.282 18	0.0
15	173.118 36	71.4	173.177 04	173.247 36	20.8
14ts	172.978 09	67.8	173.037 93	173.107 57	104.9
16	173.069 41	68.6	173.125 78	173.197 04	1.1
17	173.043 84	68.7	173.100 71	173.177 48	13.5
18	173.073 02	72.0	173.131 48	173.204 19	0.0

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

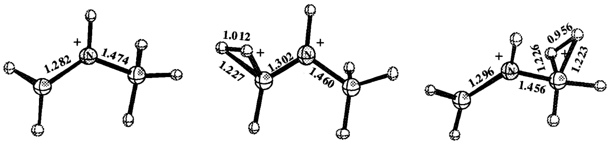
of 0.96.[7] For the MP2/6-31G**-optimized structures, further geometry optimizations were carried out at the MP2/6-311+G** level. For improved energy, single-point energies at MP4(SDTQ)/6-311+G** on MP2/6-311+G**-optimized geometries were computed. Final energies were calculated at the MP4(SDTQ)/6-311+G**//MP2/6-311+G** + ZPE level. Atomic charges and Wiberg bond index[8] bond order were obtained using the natural bond orbital analysis (NBO)[9] method at the MP2/6-311+G**//MP2/6-311+G** level. Calculated energies are given in Table 1. MP2/6-311+G**-optimized geometrical parameters and final energies will be discussed throughout, unless stated otherwise. NMR chemical shifts were calculated by the GIAO method.[10] GIAO-MP2[11] calculations using the tzp/dz basis set[11,12] have been performed with the ACES II program.[13] The ^{13}C and ^{15}N NMR chemical shifts were referenced to TMS [calculated absolute shift i.e $\sigma(C) = 198.8$) and NH_3 ($\sigma(N) = 280.5$]. Calculated chemical shifts are listed in Figure 6.



1 C_s (17.9) **2** C_s (6.0) **3** C_1 (15.2)

4 C_s (0.0)

FIGURE 1. MP2/6-311+G** structures (relative energies in kcal/mol given in parentheses) of **1**−**4**.



5 C_s (0.0) **6** C_s (34.5) **7** C_1 (6.1)

FIGURE 2. MP2/6-311+G** structures (relative energies in kcal/mol given in parentheses) of **5**−**7**.

Results and Discussion

Ethyleniminium Ion, $CH_3CH{=}NH_2^+$ 1. Ethyleniminium ion **1** can undergo protonation on either the nitrogen, the CH carbon, or the C−H (CH_3) bond (Figure 1). Nitrogen-protonated C_s symmetrical structure **2** is a minimum on the PES. The structure **2**, an isoelectronic analogue of 2-propyl cation, is in fact a carbenium−ammonium dication. The structure contains a very short C−C bond with a length of 1.386 Å. This is because of the involvement of extensive methyl hyperconjugation to stabilize the adjacent highly electron deficient carbenium ion center, since the formal positive charge bearing carbenium and ammonium centers is adjacent. Deprotonation of **2** is computed to be endothermic by 11.9 kcal/mol.

The C−H (CH) protonated ethyleniminium ion does not correspond to a minimum and dissociates into methyleneiminium ion ($CH_2{=}NH_2^+$) and methyl cation (CH_3^+) upon optimization. However, C−H (CH_3) protonated form **3** does correspond to a minimum. The structure **3** contains a pentacoordinate carbon with a 3c−2e bond. Unlike **2**, the formal positive-charge-bearing centers of **3** are separated by one carbon. Despite this, the structure **3** is 9.2 kcal/mol less stable than **2** (Table 1).

However, we found that the global minium is not the structure **2**, but the isomeric structure **4** is. The structure **4** is 6.0 kcal/mol more stable than **2**.

N-Methylmethyleniminium Ion, $CH_2{=}NHCH_3^+$ 5. We have calculated the structures of protonated *N*-methylmethyleniminium ion (Figure 2). The nitrogen-protonated structure does not correspond to a minimum and dissociated into methyleneiminium ion ($CH_2{=}NH_2^+$) and methyl cation (CH_3^+) upon optimization. The C−H (CH_2) protonated structure **6** is a minimum and is characterized by a tetracoordinate carbon involving a 3c−2e bond. The C−H (CH_3) protonated **7** is also a minimum

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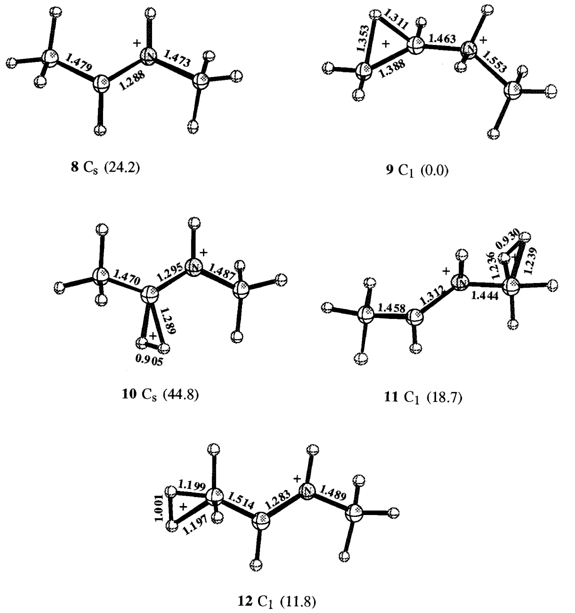


FIGURE 3. MP2/6-311+G** structures (relative energies in kcal/mol given in parentheses) of **8**−**12**.

and contains a pentacoordinate carbon with a 3c−2e bond. The structure can also be considered as a complex between methylimine ($CH_2{=}NH$) and CH_4^{2+} (protonated methyl cation). The structure **7** is substantially more stable than **6** by 28.4 kcal/mol (Table 1). Deprotonation of **7** is calculated to be exothermic by 6.1 kcal/mol.

N-Methylethyleniminium Ion, $CH_3CH{=}NHCH_3^+$ 8. Structures of protonated *N*-methylethyleniminium ion are displayed in Figure 3. Four structures, nitrogen-protonated **9** and C−H (CH) protonated **10**, C−H (CH_3-NH) protonated **11**, and C−H (CH_3CH) protonated **12**, are located as minima on the PES. Structure **9** contains a hydrogen-bridged carbocation unit away from the positively charged nitrogen center. Structure **10** is characterized by a tetracoordinate carbon involving a 3c−2e bond. On the other hand, each of the structures **11** and **12** is characterized by a pentacoordinate carbon involving a 3c−2e bond.

Energy comparison shows that the nitrogen-protonated **9** is the most stable form, followed by C−H (CH_3CH) protonated **12**. Structure **10** is the least stable isomer.

Isopropyleniminium Ion, $(CH_3)_2CH{=}NH_2^+$ 13. Two protonated isopropyleniminium ions, nitrogen-protonated **14** and C−H (CH_3) protonated **15**, were located as minima (Figure 4). The central carbon-protonated structure does not correspond to a minimum. The structure **14** contains a trivalent carbenium ion center and tetravalent ammonium ion center. Thus, the structure is a carbenium−ammonium dication. The calculated C−C and C−N distances of **14** are 1.434 and 1.484 Å, respectively.

The structure of the dication **14** is particularly interesting because it is an isoelectronic analogue of *tert*-butyl cation. The *tert*-butyl cation is stabilized not only by weak external solvation but also intramoleculary by 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 an adjacent positively charged ammonium group of **14**, electron deficiency and the reactivity of the carbocationic center would be further increased. This would lead to an enhanced reactivity of the carbocationic center. Thus, the structure **14** can be compared not with *tert*-butyl cation but with C−H protonated *tert*-butyl dication **V** (Scheme 3).[14] Olah et al. have been able to show[14] by hydrogen/deuterium exchange experiments and theoretical studies that long-lived stable *tert*-butyl cation undergoes C−H protonation in superacids to form highly electron deficient protio *tert*-butyl dications **V**. With further protonation of *tert*-butyl cation in superacidic solutions, C−H hyperconjugative stabilization of the trivalent carbenium center is enhanced (vide supra). This leads also to an enhanced overall electron deficiency and reactivity.

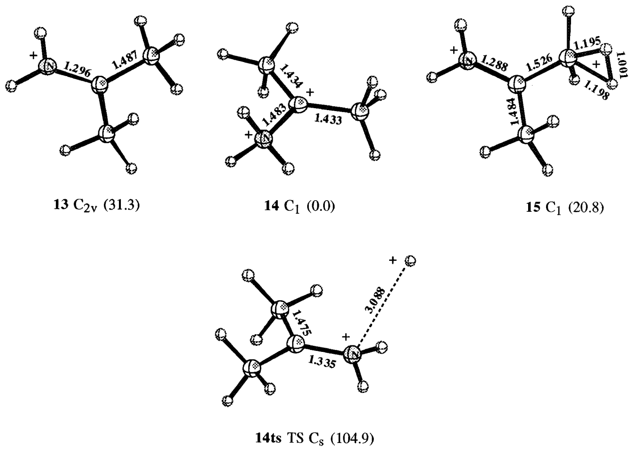


FIGURE 4. MP2/6-311+G** structures (relative energies in kcal/mol given in parentheses) of **13**−**15**.

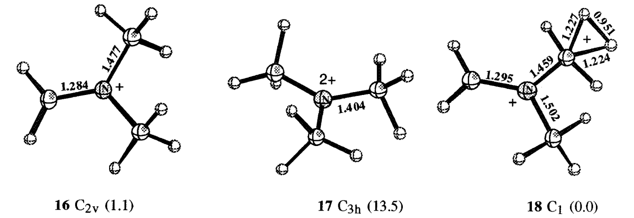
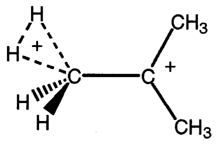


FIGURE 5. MP2/6-311+G** structures (relative energies in kcal/mol given in parentheses) of **16**−**18**.

SCHEME 3



V

The C−H (CH_3) protonated **15** is characterized with a pentacoordinate carbon involving a 3c−2e bond. Thus the structure is a carbonium−iminium dication. The structure **15** is significantly less stable than **14** by 20.8 kcal/mol. In **14**, the formal positive-charge-bearing carbenium and ammonium centers are adjacent, whereas in **15** they are separated by one carbon. Despite this, the structure **15** is significantly less stable than **14**.

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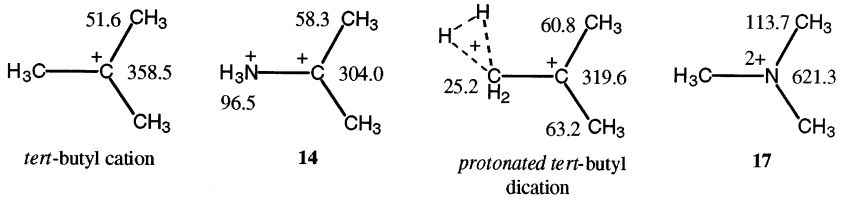

FIGURE 6. GIAO-MP2/tzp/dz//MP2/6-311+G**-calculated ^{13}C and ^{15}N NMR chemical shifts of *tert*-butyl cation, **14**, protonated *tert*-butyl cation, and **17**.

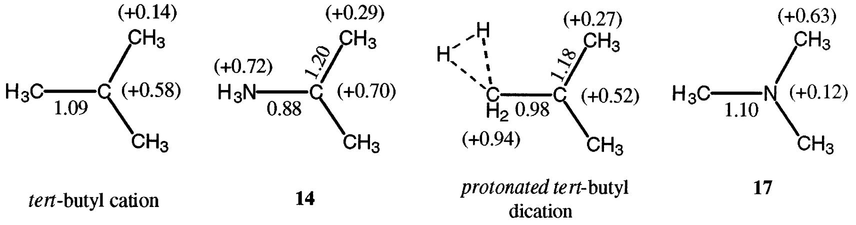

FIGURE 7. MP2/6-311+G** calculated Wiberg bond index and NBO charges (given in parentheses) of *tert*-butyl cation, **14**, protonated *tert*-butyl cation, and **17**.

Deprotonation of **14** is calculated to be substantially endothermic by 31.3 kcal/mol. We have identified the transition structure **14ts** (Figure 1) for deprotonation of **14**, which lies 104.9 kcal/mol above **14** (Table 1). Thus, the dication **14** has also a very high kinetic barrier for deprotonation. Such endothermicity and high kinetic barrier for deprotonation are also reported for guanidinium dication.[15]

***N*,*N*-Dimethylmethyleniminium Ion, $CH_2{=}N\text{-}(CH_3)_2^+$ 16.** *N*,*N*-Dimethylmethyleniminium ion and its derivatives are used in organic synthesis as Eschenmoser's salts. Protonations of *N*,*N*-dimethylmethyleniminium ion can take place on the C−H (CH_2) to give **17** and on C−H (CH_3) to give **18**. The central nitrogen-protonated form does not correspond to a minimum. Structure **17** with C_{3h} symmetry is isoelectronic with the *tert*-butyl cation and can be considered as the trimethylamine dication (Figure 5).

The structure contains a formal doubly electron deficient sp^2-type trivalent nitrogen center. On the other hand, the structure **18** is characterized by a pentacoordinate carbon involving a 3c−2e bond. Thus **18** can be considered as a iminium−carbonium dication. The structure can also be considered as a complex between *N*-methylmethylimine ($CH_2{=}NCH_3$) and CH_4^{2+}. Structure **18** is computed to be more stable than **17** by 13.5 kcal/mol (Table 1). Deprotonation of **18** is slightly endothermic (1.1 kcal/mol). Therefore, dication **17** and monocation **16** are almost isoenergetic in the gas phase. Structures **17** and **18** were found to be isostructural with the protonated isopropyleniminium dications **14** and **15**, respectively.

We have also calculated the ^{13}C and ^{15}N NMR chemical shifts of **14** and **17** by the GIAO-MP2 method using MP2/6-311+G** geometry, and these are given in Figure 6. The ^{13}C NMR chemical shifts of isoelectronic analogue *tert*-butyl cation were also calculated at the same level in order to explore the effect of an additional charge in dications **14**. The calculated ^{13}C NMR shift of the central carbenium carbon of *tert*-butyl cation is δ 358.5 [wrt $(CH_3)_4Si$)], which is 23.3 ppm deshielded compare to that of the experimental value of δ 335.2.[16] The calculated ^{13}C chemical shift of the central carbenium carbon of **14** (δ 304.0) was found to be 54.5 ppm shielded compared to the calculated value of *tert*-butyl cation. For comparison, ^{13}C NMR chemical shifts of the central carbenium carbon of protonated *tert*-butyl dication were also calculated and found to be δ 319.6, which is also 39.0 ppm shielded compare to that of the calculated value of *tert*-butyl cation. Such ^{13}C NMR shieldings in the dications compared to the monocation can be rationalized by the enhanced dissipation of the positive charge by hyperconjugative effects. This can be noticed by the computed NBO charges[9] (see Figure 7). The charge of the carbenium carbon of the *tert*-butyl cation (+0.58 au) is slightly more positive than that of the protonated *tert*-butyl dication (+0.52 au). In *tert*-butyl dication, each of the CH_3 groups as a whole bears +0.14 au charge. Whereas in protonated *tert*-butyl dication, each of the CH_3 groups as a whole bears +0.27 au charge. This indicates enhanced dissipation of the positive charge in the dication. These results are also consistent with the calculated Wiberg bond index[8] (Figure 7). The calculated ^{15}N NMR chemical shift of NH_3 nitrogen of **14** was found to be δ 96.5 (wrt NH_3). The correlated GIAO-MP2-calculated ^{15}N NMR chemical shifts, however, can differ significantly from experimental values, because the accurate calculation requires an extensive electron correlation treatment such as that provided by the CCSD(T) method.[11b,17−19] The ^{15}N NMR chemical shift of the central nitrogen of **17** is calculated to be highly deshielded at δ 621.3. The ^{13}C NMR chemical shift of the methyl carbon of **17** is also calculated to be quite deshielded at δ 113.7.

We have previously reported[3,14,20,21] that superelectrophilic interactions offer an adequate explanation for the observed experimental data for a variety of superacid-

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catalyzed reactions. Our present studies will help in understanding the nature of such interactions of methyl- and dimethylmethyleniminium ions with acids, superacids, and electrophiles. If the nitrogen atoms and C−H bond of methyleniminium ions are further protonated, the electron deficiency of the systems would become more pronounced, resulting in enhanced reactivity.[3] In the limiting case, this could lead to dicationic superelectrophiles.[3]

Conclusion

Structures and energies of superelectrophilic dications derived by protonation of methyl- and dimethylmethyleniminium ions were calculated at the MP2/6-311+G** level. These calculations show that the dications such as N-protonated isopropyleniminium **14** are minima on the potential energy surface. Deprotonation energies of the global minimum structures were also calculated. The ^{13}C NMR chemical shifts of the intriguing dication **14** were calculated using the GIAO-MP2 method. The ^{13}C NMR chemical shifts of isoelectronic analogue *tert*-butyl cation were also calculated at the same level in order to explore the effect of an additional charge in dications **14**.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

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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