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Bridgehead Adamantyl, Diamantyl, and Related Cations and Dications[1a]

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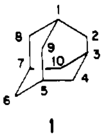
Abstract: The bridgehead 1-adamantyl cation **3a** and a series of methyl-substituted adamantyl cations **3b-d** have been prepared in superacid medium and characterized by ^1H and ^{13}C NMR spectroscopy. The relative deshielding of bridgehead γ carbons with respect to β-methylenes has been rationalized in terms of a C–C hyperconjugative effect. The cation generated from the ionization of *exo*-5,6-trimethylene-2-norbornyl derivatives has been shown to be the equilibrating 2,3-trimethylene-2-norbornyl cation **12**. The temperature-dependent ^{13}C NMR spectroscopic studies on **12** indicate the barrier for the degenerate *exo*-2,3-hydrogen shift, $\Delta G^{\ddagger} = 7.2$ kcal/mol. The cation **12** in a solution of SO_2ClF is stable even at room temperature; however, in a solution of SO_2, it smoothly and irreversibly rearranges to bridgehead 1-adamantyl cation **3a**. On the other hand, 2-methyl-5,6-*exo*-trimethylene-2-norbornyl cation **17** was found to be quite stable. The 1-adamantyl cation was also studied as its isolated SbF_6^- salt by solid-state CPMAS ^{13}C NMR spectroscopy. The bridgehead 1- and 4-diamantyl cations **4** and **27** were also prepared and studied. Heteronuclear-correlated 2D NMR spectra were also obtained for **3a** and **4** and used in many assignments of the NMR shifts. Cation **27** slowly and irreversibly rearranges to **4**. The cation **4** was also generated by the ionization of 3-diamantyl derivatives. The above rearrangements to the thermodynamically more stable ion **4** has been rationalized in terms of facile intermolecular hydrogen shifts rather than intramolecular shifts. The bridgehead diamantyl cations **4** and **27** also derive their stability from C–C hyperconjugative effects similar to their adamantyl analogues. In contrast to the instability of secondary 3-diamantyl cation the corresponding 3-methyl- and 3-phenyl-substituted analogues were found to be rather stable. 3,3′-(1,1′-Biadamantyl) dication **6** and 4,9-diamantyl dication **5** were also generated and studied. The C–C hyperconjugative stabilizing interaction which is found "operative" in all of the bridgehead cations including dication **6** is absent in the 4,9-diamantyl dication **5**. Charge–charge repulsion in **5** seems to diminish such C–C hyperconjugative interaction. All attempts to prepare the 1,3-adamantyl dication **8** or the 1,6-diamantyl dication **7** were unsuccessful.

Over the past 2 decades, extensive research has been carried out pertaining to the chemistry of adamantane, diamantane, and other so-called diamondoid molecules.[2,3] The unique structural features of adamantane (**1**) and diamantane (**2**) are also ideal for a systematic study of their cations, relating to both structure and chemical reactivity. The tight interlocking of cyclohexane rings into rigid, relatively strain-free chair conformations allows no easy formation of double bonds and no back-side (electrophilic or nucleophilic) attack.



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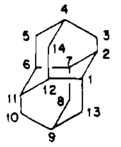

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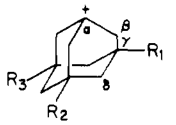
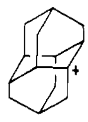
In our preliminary work, the preparation and study of the 1-adamantyl cation **3a** and the 1-diamantyl cation **4** were reported. They were characterized by ^1H NMR spectroscopy.[4,5] We now wish to describe in detail the preparation and ^1H and ^{13}C NMR spectroscopic characterization of bridgehead adamantyl, substituted adamantyl, related bridgehead diamantyl, and 3-substituted diamantyl cations. Studies relating to the formation of **3a** from trimethylenenorbornyl derivatives have been included along with the cross-polarization magic angle spinning ^{13}C NMR spectroscopic study of **3a** in its crystalline state (as its SbF_6^- salt). The ^{13}C and ^1H NMR chemical shifts in **3a** and **4** were also cross-correlated by using heteronuclear correlated two-dimensional (2D NMR) spectra. We also describe the preparation and spectroscopic characterization of the related 4,9-diamantyl dication **5** (congressane dication) and the 3,3′-(1,1′-biadamantyl) dication **6**. Attempted preparation of the 1,6-diamantyl dication **7** and the 1,3-adamantyl dication **8** were, however, unsuccessful.



3a: $R_1 = R_2 = R_3 = H$
3b: $R_1 = CH_3$; $R_2 = R_3 = H$
3c: $R_1 = R_2 = CH_3$; $R_3 = H$
3d: $R_1 = R_2 = R_3 = CH_3$



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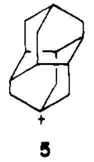

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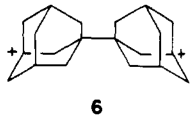

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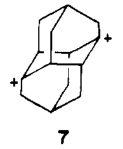

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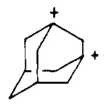

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Results and Discussion

1-Adamantyl Cation 3a and Related Methyl-Substituted Cations (3b–d). The bridgehead 1-adamantyl cation **3a** can be readily prepared by treating adamantane (**1**) with superacids

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(1) (a) Stable Carbocations. 258. For part 257, see: Krishnamurthy, V. V.; Iyer, P. S.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 7068. (b) University of Southern California. (c) Case Western Reserve University. (d) Visiting Scientist from the University of Szeged, Hungary. (e) Princeton University. (f) Friedrich-Alexander Universitat, Erlangen, Nurnberg.

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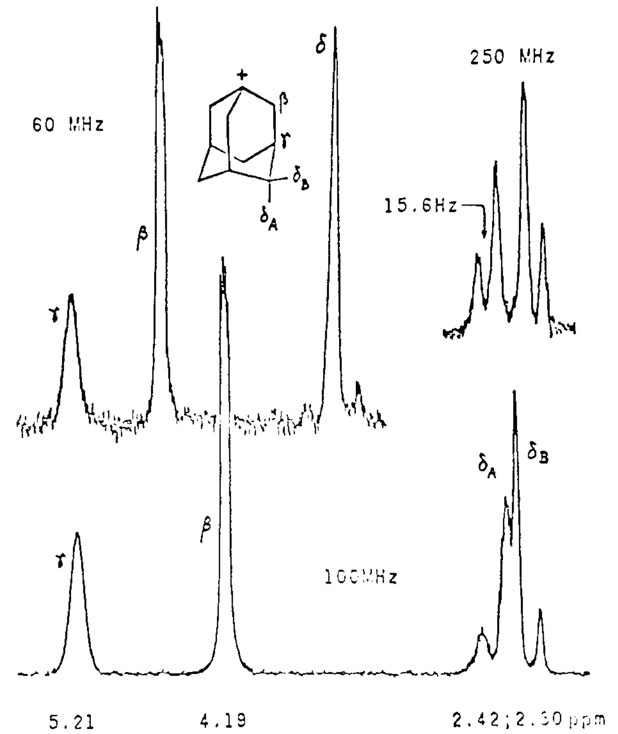
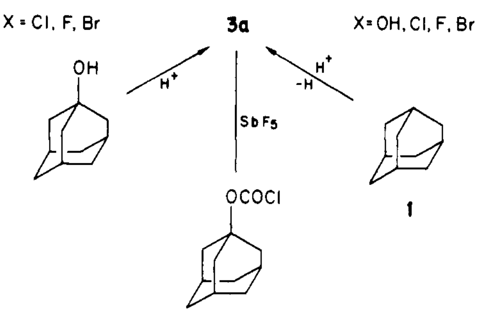


Figure 1. ^{1}H NMR spectrum of 1-adamantyl cation **3a** at (a) 14.09 kG (60 MHz), (b) 23.48 kG (100 MHz), and (c) 58.70 kG (250 MHz).

(FSO_3H/SbF_5 or HF/SbF_5) with or without low nucleophilicity solvents (SO_2 or SO_2ClF). The ion **3a** can also be generated from a variety of precursors including 1- and 2-substituted adamantanes.[6-8] The mechanism of the rearrangement of the 2-adamantyl cation formed as an intermediate in the latter case has been discussed earlier.[8,9]



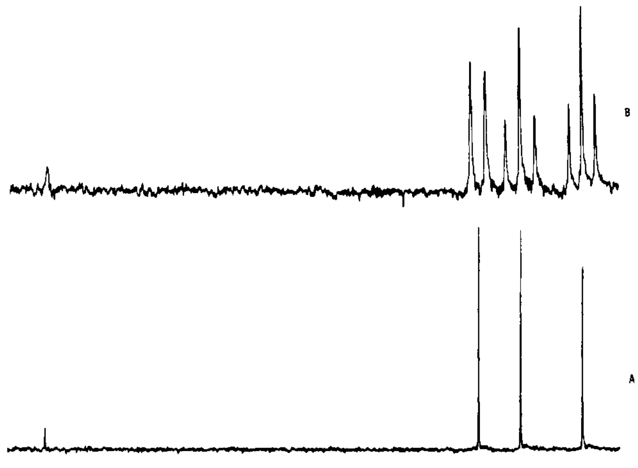
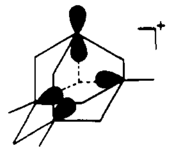


Figure 2. ^{13}C NMR spectra (20 MHz) of 1-adamantyl cation **3a** in SbF_5/SO_2ClF solution at −80 °C: (A) proton decoupled; (B) proton coupled.

Of particular interest is the generation of **3a** starting from 2-*exo*-(chloro)hydroxy-*exo*-trimethylenenorbornane in SbF_5/SO_2 solution at temperatures above −30 °C (vide infra).[7]

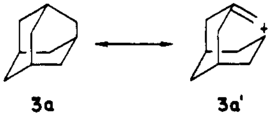
The 60-MHz ^{1}H NMR spectrum of the 1-adamantyl cation **3a** (Figure 1) consists of three unresolved multiplets at δ 2.30 (6 H), 4.19 (6 H) and 5.19 (3 H) (Table I). The relative intensities of the signals require assignment of the lowest field peak to the γ (bridgehead) protons. This indicates that β protons which are nearest to the (formal) positive charge are not as deshielded as the γ protons. A better resolved spectrum is obtained at 100 MHz, wherein the δ protons are observed as an AB pattern. At 250 MHz, this AB pattern is well resolved and J_{AB} = 15.6 Hz.

The unusual fact that in the 1-adamantyl cation **3a** the γ protons absorb at a lower field than the β ones has been explained in terms of a cage effect.[9] Originally, this effect was interpreted[4] in terms of an interaction of the "empty" p orbital of the trivalent carbocation center with the back lobes of three sp^3 bridgehead C–H orbitals which converge toward the (tetrahedral) center of the molecule. This geometrically favored overlap would account for selective sharing of the positive charge by the bridge-head positions. Indeed extended Hückel calculations suggest stabilization to the extent of 1.2 kcal/mole for such interactions.[10,11]



3a

However, subsequent MO calculations by Hoffmann, Gleiter, and Heilbronner[12-14] indicated that such interactions are unlikely in adamantyl systems wherein the overlapping orbitals are intervened by only two bonds. More recent work by Sunko and Hehre[15] has pointed out that resonance structures such as **3a** ↔ **3a′** are responsible for the γ-deshielding effect. In a way this can



3a **3a′**

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Table I. ^1H NMR Chemical[a] Shifts of Adamantyl, Diamantyl, Trimethylenenorbornyl, and Related Cations and Dications

cation or dication	temp, °C	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}	H_{11}	H_{12}	H_{13}	H_{14}	others
3a	−80		4.19	5.19	2.30	5.19	2.30	5.19	4.19	2.30	4.19					
3b	−80		3.79		1.85	5.00	2.13	5.00	4.09	2.13	4.09					CH_3 = 1.57
3c	−80		3.81		1.91		1.99	4.86	4.03	1.99	4.03					CH_3 = 1.71
3d	−80		3.77		1.93		1.93		3.77	1.93	3.77					CH_3 = 1.69
12	−60	4.18	2.80	2.80	4.18	br	br	1.65 1.50	3.40 2.80	2.36	3.40 2.80					
6	−80		3.79		4.16	5.04	2.05 (J_{H-H} = 12 Hz)	5.04	2.20 (J_{H-H} = 12 Hz)	2.20 (J_{H-H} = 12 Hz)	4.16					
4	−80		4.10	2.00 1.70 (J_{AB} = 18 Hz)	2.00	1.90	2.00	4.67	2.30 2.10 (J = 16 Hz)	4.40	2.30 2.10 (J = 16 Hz)	4.67	4.10	3.50	2.00 1.70 (J_{AB} = 18 Hz)	

Table II. ^{13}C NMR Chemical Shifts[a] of Adamantyl, Diamantyl, and Trimethylenenorbornyl Cations and Related Dications

cation or dication	temp, °C	chemical shifts, ppm														others
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	
3a	−80	300	65.7 (J_{C-H} = 147.6 Hz)	86.8	34.5	86.8 (J_{C-H} = 149.8 Hz)	34.5	86.8	65.7	34.5 (J_{C-H} = 129.5 Hz)	65.7					
3b	−80	298.7	73.2 (J_{C-H} = 142.4 Hz)	99.2	42.8 (J_{C-H} = 129.5 Hz)	84.6 (J_{C-H} = 153.4 Hz)	35.8 (J_{C-H} = 130.6 Hz)	84.6	66.7 (J_{C-H} = 149.2 Hz)	42.8	66.7					CH_3 = 29.6 (J_{C-H} = 130.5 Hz)
3c	−80	296.2	71.8	94.0	49.1	94.0	41.8	79.9	65.4	41.8	71.8					CH_3 = 30.3
3d	−80	294.1	71.0	89.9	48.6	89.9	48.6	89.9	71.0	48.6	71.0					CH_3 = 30.1 (J_{C-H} = 128.6 Hz)
12	−29	59.7	32.6	32.6	59.7	194.0 (J_{C-H} = 62 Hz)	194.0	31.4	46.1	28.7	46.1					
	−130[b]	70.3		br		309.6	79.2		br							
17	−80	81.5	298.2	60.7	44.6	34.7	55.4	36.1	28.9	28.9	31.9					CH_3 = 31.9
6	−80	99.3	61.0	300.9	68.6	82.9	34.8	82.9	36.1	36.1	68.6					
4	−80	297.9	70.5	35.1	22.7	36.1	37.7	95.3	32.3	80.6	32.3	95.3	70.5	63.1	35.1	
27	−90	37.6	91.7	63.7	305.1	63.7	91.7	37.6	30.9	21.4	30.9	37.6	91.7	30.9	63.7	
5	−80	78.8	78.8	58.6	337.3	58.6	78.8	78.8	58.6	337.3	58.6	78.8	78.8	58.6	58.6	
31	−80	64.7	64.7	51.4	230.9	51.4	64.7	64.7	51.4	230.9	51.4	64.7	64.7	51.4	51.4	
33-F	−80[b]	294.5		br	br	br	br	93.9	br	br	br	93.9	br	br		
34-CH_3	−80	53.7	73.5	312.4	59.3	47.5	34.5	53.7	33.9	22.0	32.7	34.2	34.5	33.9	47.5	CH_3 = 37.9
34-C_6H_5	−80	49.7	59.3	265.1	46.1	45.7	34.5	49.7	35.6	22.8	33.7	34.5	34.5	35.6	45.7	ar, C_p = 151.2, C_o, $C_{o'}$ = 136.1, 135.9; C_i = 134.9; C_7 = 130.7

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[a] Chemical shifts are in ppm from external capillary tetramethylsilane. [b] Many peaks are too broad to assign.

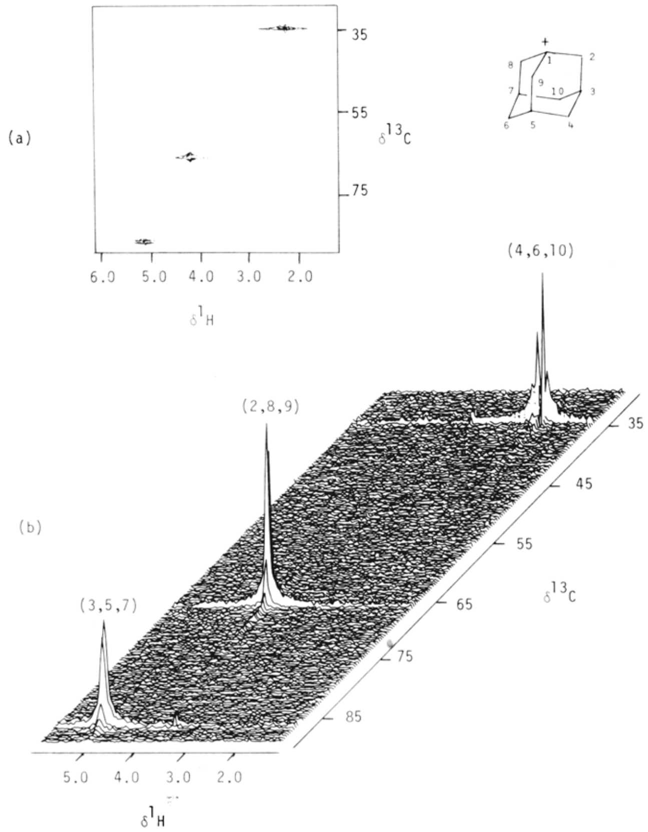


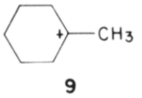
Figure 3. ^{1}H–^{13}C chemical shift correlated 2D NMR spectrum of 1-adamantyl cation in SbF_3/SO_2 at −30 °C: (a) contour plot; (b) stacked plot.

be considered as a carbon–carbon hyperconjugation effect.

A similar γ-hydrogen deshielding effect is observed in 3-methyl-1-adamantyl cation **3b** and 3,5-dimethyl-1-adamantyl cation **3c** prepared from their bromo precursors (δ 5.00 for **3b** and 4.86 for **3c**), although in the latter two cations the charge is more delocalized on to the methyl-substituted bridgehead carbons.

These effects are more pronounced in the ^{13}C NMR spectra of these cations. The 20-MHz ^{13}C NMR spectrum of **3a** (Figure 2) in SbF_5/SO_2ClF solution shows the following absorptions: δ ^{13}C 300 (s), 86.8 (d, $J_{C-H} = 149.8$ Hz), 65.7 (t, $J_{C-H} = 147.6$ Hz), and 34.5 (t, $J_{C-H} = 129.5$ Hz). From the multiplicity data the chemical shifts can be readily assigned to C_α,C_γ, C_β, and C_δ carbons, respectively.

The assignment of the ^{13}C resonances in **3a** were also correlated to their earlier assigned ^{1}H resonances by obtaining its heteronuclear correlated 2D NMR spectrum[16] (Figure 3), recorded in SbF_5/SO_2 at −40 °C. Figure 3 clearly indicates that the carbon resonating at δ ^{13}C 86.8 (d) is attached to a proton resonating at δ ^{1}H 5.19 (3 H). Similarly the carbon resonance at δ ^{13}C 65.7 (t) can be correlated to the proton resonance at δ ^{1}H 4.19 (6 H) and the carbon resonance at δ ^{13}C 34.5 (t) to the ^{1}H AB quartet resonating at δ ^{1}H 2.30 (6 H). These correlations observed in the 2D NMR spectrum further prove the ^{13}C and ^{1}H NMR chemical shift assignments in **3a**. The observation of a greater deshielding of the more distant C_γ carbons than the C_β carbons which are adjacent to the carbocationic center is noteworthy. Also the $C_\alpha{}^+$ carbocationic shift of δ 300 is more shielded than that in the model 1-methyl-1-cyclohexyl cation **9**.[17] The ^{13}C NMR chemical shift shielding of $C_\alpha{}^+$ and deshielding of C_γ is again best rationalized by the previously discussed carbon–carbon hyperconjugation effect.[15] It is interesting to note that C_γ's are deshielded by 64.4 ppm, while C_β's are deshielded by only 38.0 ppm in the 1-adamantyl cation **3a** compared to adamantane (**1**).



$\delta\ ^{13}C^+$ 329.4

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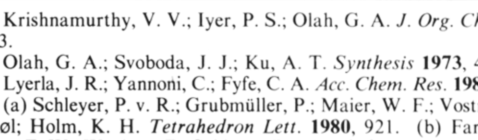
These effects are even more pronounced in the case of 3-methyl-, 3,5-dimethyl-, and 3,5,7-trimethyl-1-adamantyl cations (**3b**,**c**, and **d**, respectively). The $C_\alpha{}^+$ carbocationic center is progressively shielded in their ^{13}C NMR spectra. The chemical shifts range from δ 298.7 in **3b** to δ 294.1 in **3d** (δ 296.2 in **3c**). The gradual shielding of $C_\alpha{}^+$ is due to the progressive methyl substitution at the bridgehead carbons. In fact, the bridgehead carbon (C_3) bearing the methyl group in **3b** is observed at δ 99.2 due to the methyl substituent effect as well as γ-carbon deshielding effect due to C–C hyperconjugation.[15] In fact, in the neutral hydrocarbon series, one observes a deshielding of the γ carbons by only 1.4 ppm between adamantane and 1-methyladamantane.[18] Similarly, the chemical shifts of C_3,C_5 and C_3,C_5,C_7 carbon atoms are also deshielded in **3c** and **d**, respectively (δ 94.0 and 89.9). The above observations again support the importance of mesomeric form **3a′** in stabilizing the bridgehead 1-adamantyl cation **3a** and related substituted adamantyl cations (**3b–d**).

We have also extended our studies to the isolation of the 1-adamantyl cation **3a** as its SbF_6^- salt and its solid-state ^{13}C NMR spectrum. We obtained 50-MHz magic angle spinning cross-polarization ^{13}C NMR spectrum of the bridgehead 1-adamantyl cation **3a** at room temperature. The SbF_6^- salt was prepared from 1-fluoroadamantane by using previously published procedure.[19] Except for some line broadening (line widths = ~50–80 Hz), the solid-state ^{13}C NMR spectrum is almost identical with the solution spectrum in SbF_5/SO_2ClF solution. The chemical shifts obtained in the solid state are δ ^{13}C 300, 89.7, 67.5, and 36.5. Apparently the dipolar interaction of the fluorines of the SbF_6^- counterion which results in a certain amount of line broadening did not cause much interference in the solid-state study. Other workers have circumvented this problem by broad-band fluorine decoupling,[20] adaptable, however, for only specialized instrumentation operating at low temperatures to dissipate excessive heat generated during decoupling.

Study of the Formation of the 1-Adamantyl Cation 3a from Trimethylenenorborane. The acid-catalyzed isomerization of isomeric trimethylenenorbornanes to adamantane (**1**) not only opened up the chemistry of adamantanoid compounds but also represents one of the most fascinating intramolecular rearrangements known in carbocation chemistry.[2a–c] The mechanism of the rearrangement process has been studied in significant detail;[21] however, the possible direct observation of intermediate carbocations along the isomerization path remained a longstanding challange.



In SbF_5/SO_2 solution at −78 °C, 2-*exo*-chloro-5,6-*exo*-trimethylenenorbornane (or 2-Br, 2-OH) first gave an intermediate cation **10**, which then rearranges to bridgehead 1-adamantyl cation **3a** around −30 °C. The solution of **10** kept below −50 °C in SbF_5/SO_2 gave upon hydrolysis a single alcoholic product identified as 2,3-*endo*-trimethylene-2-*exo*-norbornanol (**11**).[22a] When

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(17) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1978**, *100*, 1487.

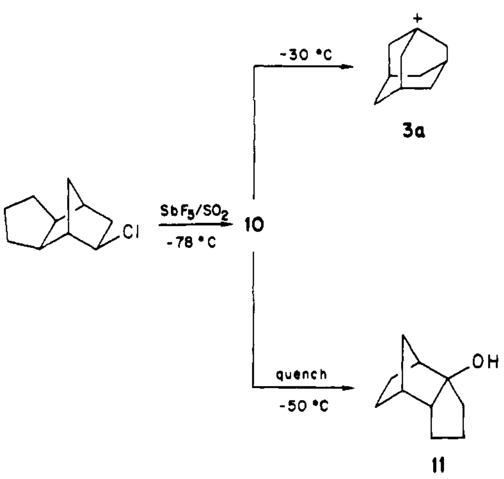
(18) Krishnamurthy, V. V.; Iyer, P. S.; Olah, G. A. *J. Org. Chem.* **1983**, *48*, 3373.

(19) Olah, G. A.; Svoboda, J. J.; Ku, A. T. *Synthesis* **1973**, 492.

(20) Lyerla, J. R.; Yannoni, C.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15*, 208.

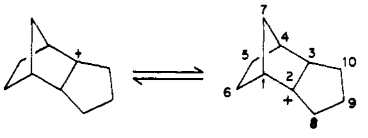
(21) (a) Schleyer, P. v. R.; Grubmüller, P.; Maier, W. F.; Vostrowski, O.; Skattebøl; Holm, K. H. *Tetrahedron Lett.* **1980**, 921. (b) Farcasiu, M.; Hageman, E. W.; Wenkert, E.; Schleyer, P. v. R. *Ibid.* **1981**, 1505. (c) Jäggi, F. G.; Ganter, C. *Helv. Chim. Acta* **1980**, *63*, 866. (d) Klester, A. M.; Jäggi, F. G.; Ganter, C. *Ibid.* **1980**, *36*, 1291. (e) Klester, A. M.; Ganter, C. *Ibid.* **1983**, *66*, 1200.

(22) (a) The structure is tentatively assigned as **11** (endo, exo stereochemistry) based on its ^{13}C NMR spectrum. (b) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026.



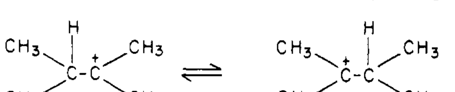
the ionization was carried out in SbF_5/SO_2ClF solution, the intermediate ion **10** was stable and did not rearrange to **3a** even at room temperature (25 °C) in a sealed NMR tube. The same ion **10** was obtained from various *exo*- or *endo*-trimethylenenorbornyl precursors.

The intermediate **10** generated in either SbF_5/SO_2 or SbF_5/SO_2ClF showed identical ^1H and ^{13}C NMR spectra. The 60-MHz ^1H NMR spectrum of **10** at -60 °C in SbF_5/SO_2ClF solution consists of proton absorptions at δ 4.18 (2 H, br s), 3.40 (2 H, br), 2.80 (6 H, br), 2.36 (2 H, br s), 1.65 (1 H), and 1.50 (1 H, s). However, it was found that the ^1H NMR spectrum was temperature-dependent. The quenching experiments does indicate that the structure of **10** probably is **12**. The 20-MHz ^{13}C NMR spectrum does support the structure **12**. At -29 °C, ion **10** in SbF_5/SO_2ClF shows the following absorptions: δ ^{13}C 194.0 (d, J_{C-H} = 62 Hz), 59.7 (d), 46.1 (t), 32.6 (t), 31.4 (t), and 28.7 (t). The observation of six peaks and the multiplicity data clearly support the equilibrating structure **12**. The observation of the most deshielded peak at δ ^{13}C 194.0 indicates a tertiary carbocationic center equilibrating with a secondary carbon atom, and the coupling of 62 Hz is an average of a secondary C–H coupling constant and a long-range tertiary C–C–H coupling. Similar chemical shifts have been observed, for example, in 2,3-dimethyl-2-butyl cation **13**.[22b]



12

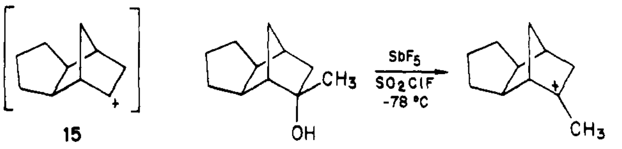
When the solution was cooled, the peaks at δ ^{13}C 194, 59.7, 46.1, and 32.6 broaden and merge into the base line, whereas the peaks at δ ^{13}C 31.4 and 28.7 remain relatively sharp. At -130 °C, the peak at δ ^{13}C 194 is split into two peaks at δ ^{13}C 309.6 and 79.2. The rest of the spectrum is too broad for proper assignments. This indicates that at this low temperature, the 1,2-hydride shift in **12** is frozen and a static (on the NMR time scale) 2,3-trimethylene-2-norbornyl cation **12** is obtained. From the temperature-dependent ^{13}C NMR spectra between -29 and -130 °C, the coalescence temperature for the C_1 and C_4 carbons was found to be -110 °C. From the frequency spearation between C_1 and C_4 carbons ($\Delta\delta$) and coalescence temperature, an approximate energy barrier[23a] of $\Delta G^{\ddagger}$ = 7.2 ± 0.5 kcal/mol for the 2,3-*exo*-hydride shift in **12** can be estimated. This value agrees very well with the barrier for the 2,3-*exo*-hydride shift in 2,3-dimethyl-2-norbornyl cation **14** estimated by Sorensen[23b] ($\Delta G^{\ddagger}$ = 7.2 kcal/mol).



δ $^{13}C_{qv}^{+}$ 197.0 (J_{CH} = 65 Hz)

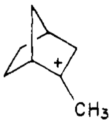
13

These observation indeed show that the structure of intermediate **10** is in fact **12**.[23c] To ascertain whether it is possible to obtain the 5,6-trimethylene-2-norbornyl cation **15**, we carried out ionization of 2-*exo*-chloro-5,6-*exo*-trimethylenenorbornane in SbF_5/SO_2ClF solution at -130 °C. However, even at this temperature, only ion **12** was observed. On the other hand, ionization of 2-*exo*-methyl-5,6-*exo*-trimethylene-2-norbornanol (**16**) in SbF_5/SO_2ClF at -78 °C gave 2-methyl-5,6-trimethylene-2-norbornyl cation **17**.

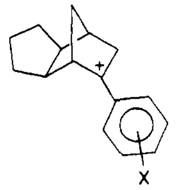


15 16 17

The 20-MHz ^{13}C NMR spectrum of **17** showed nine absorptions at δ ^{13}C 298.2 (s), 81.5 (d), 60.7 (t), 55.4 (d), 44.6 (d), 36.1 (t), 34.7 (d), 31.9 (t, q), and 28.9 (t). The C_2, C_1, and C_3 carbons can readily be assigned to δ ^{13}C 298.2, 81.5, and 60.7, respectively. It is instructive to compare these chemical shifts with those of the analogous 2-methyl-2-norbornyl cation **18**,[24a] wherein the corresponding C_2, C_1 and C_3 carbons are observed at δ ^{13}C 271.1, 80.3, and 55.6, respectively. The differences in chemical shifts can be readily retionalized by the partial σ-bridged nature of **18**.[24b] A recent study of the application of Gassman–Fentiman tool of increasing electron demand by Farnum[25] on substituted 2-aryl-5,6-trimethylene-2-norbornyl cations **19-X** does indeed indicate less σ-bridging than in the corresponding 2-norbornyl cations. Consequently the parent ion **15** should also be less σ-bridged as the secondary 2-norbornyl cation **20**. However, the parent secondary cation **15** could not be prepared under stable ion conditions. The tertiary tricyclic cation **17** was found to be quite stable even at room temperature.



18



19-X

20

An unanswered question of the present study is why ion **12** rapidly rearranges to **3a** in SO_2 solution and stays unrearranged in SO_2ClF solution. The difference in nucleophilicity and thus the solvating ability between SO_2 and SO_2ClF may be responsible for this behavior.

3,3′-(1,1′-Biadamantyl) Dication 6 and Attempted Preparation of 1,3-Adamantyl Dication 8. The bridgehead dication **6** was obtained by dissolving 1,1′-biadamantane (**21**) in SbF_5/SO_2ClF. The dication **6** was also obtained by the ionization of 3,3′-dibromo-1,1′-biadamantane (**22**) under similar conditions. It is interesting to note that **6** did not undergo protolytic cleavage at the 1,1′-bond to yield **3a** even in FSO_3H/SbF_5 solution. The ^1H and ^{13}C NMR data of **6** are given in Tables I and II.

In the ^{13}C NMR spectrum **6** shows seven absorptions characteristic of a monosubstituted bridgehead adamantyl cation. The two positive charges in **6** are significantly removed from each other (four carbons apart). The C_3 cationic center at δ 300.9 is close to those observed for **3a** and **b**.

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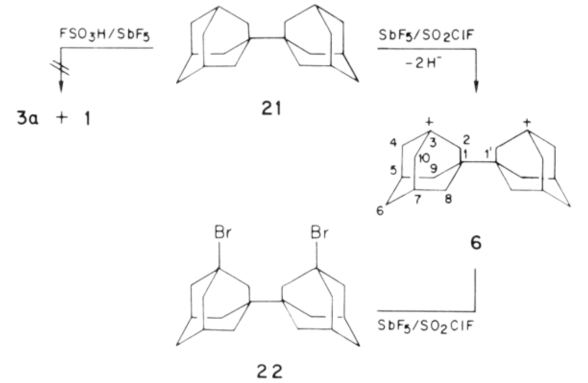
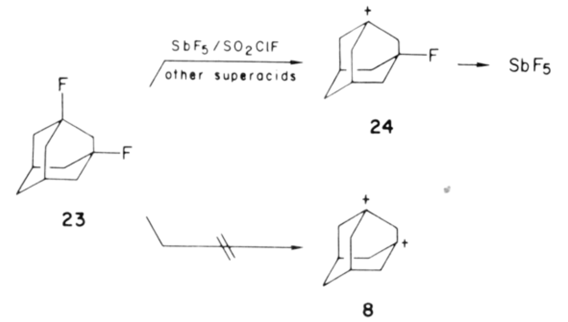
(23) (a) Sandstrom, J. "Dynamic NMR Spectroscopy"; Academic Press: New York, 1982. (b) Sorensen, T. S. *Acc. Chem. Res.* **1976**, *9*, 257. (c) Similar observations on **12** have been made by T. S. Sorensen (private communication).

(24) (a) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 5683. (b) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

(25) Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847.



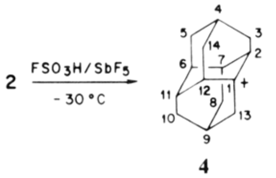
We also attempted to prepare the 1,3-adamantyl dication **8** from 1,3-difluoroadamantane (**23**) in a variety of superacid systems.



In all cases, however, only the monocation monodonor–acceptor complex **24** was obtained. These results indicate that the presence of two positive charges at the bridgehead positions separated by only one carbon atom would be too repulsive to allow formation of a stable dication. Earlier it has been demonstrated that alkyl-substituted trivalent dications can be generated only if the cationic centers are separated by at least two carbon atoms.[26]

Bridgehead Diamantyl Cations. Diamantane (**2**) can be viewed as the union of two adamantane units. Unlike adamantane (**1**), diamantane (**2**) (pentacyclo[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]tetradecane), also called congressane,[27] after the emblem of the 1963 IUPAC congress which challenged its synthesis, contains two different types of tertiary hydrogen atoms (two apical bridgehead hydrogen atoms at the 4 and 9 positions and six belt hydrogen atoms at the 1,2,6,7,11, and 12 positions). It has been found that the belt position is more reactive than the apical centers in bromination reactions.[28]

In line with the above reaction, dissolution of diamantane (**2**) in neat FSO_3H/SbF_5 results in the ionization of a belt hydrogen atom to give the 1-diamantyl cation **4**.[5] The structure of **4** was



readily assigned based on the observed symmetry in the ^1H NMR spectrum (Table I).

In analogy to the 1-adamantyl cation **3a**, the tertiary H_7 and H_{11} atoms are assigned to the lowest field peak (δ 4.67) followed by tertiary H_9 atom at δ 4.40. Of the α-hydrogen atoms H_2 and H_{12} appear at δ 4.10 followed by H_{13} as a doublet at δ 3.50, coupled to H_9. All other hydrogen atoms (H_3, H_4, H_5, H_6, H_8, H_{10}, and H_{14}) appear as a multiplet centered at δ 2.03. These resonances have been resolved by using heteronuclear correlated 2D NMR, and all ^1H resonances were assigned (vide infra).

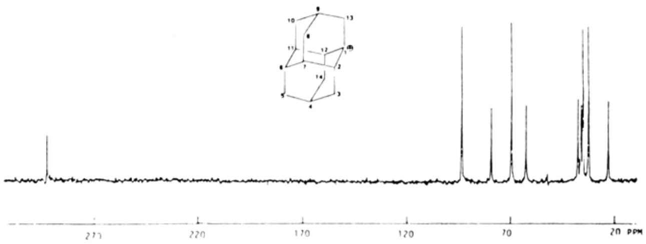


Figure 4. Proton-decoupled ^{13}C NMR spectrum (20 MHz) of 1-diamantyl cation **4** in SbF_5/SO_2ClF at −80 °C.

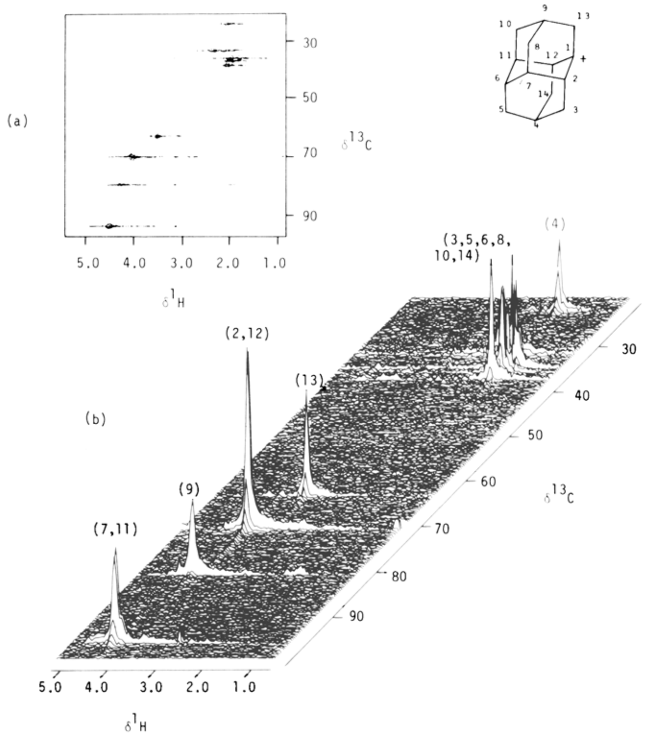
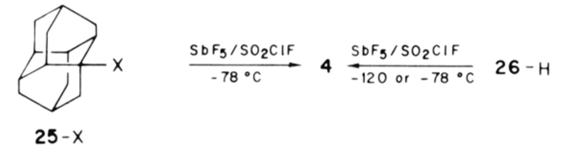


Figure 5. ^1H–^{13}C chemical shift correlated 2D NMR spectrum of 1-diamantyl cation in SbF_5/SO_2 at −30 °C: (a) contour plot; (b) stacked plot.

The 1-diamantyl cation **4** can be obtained by the ionization 1-diamantyl derivatives **25**-X (X = OH, Br, and F) in SbF_5/SO_2ClF solution.[8,9] The same ion **4** was also obtained by the



25-X

X: OH, Br, F, Cl

ionization of 3-diamantanol **26**-H in SbF_5/SO_2ClF analogous to the corresponding behavior of secondary 2-adamantyl derivatives[8] (vide infra).

The 20-MHz ^{13}C NMR spectrum of **4** (Figure 4) in SbF_5/SO_2ClF at −80 °C shows ten absorptions in agreement with its symmetry. Assignment of the individual carbons was made based on intensity and multiplicity data [and also based on its close resemblance to 1-adamantyl cation **3a**]. The chemical shifts are δ ^{13}C 297.9 (s, C_1), 95.3 (d, C_7, C_{11}), 80.6 (d, C_9), 70.5 (d, C_2, C_{12}), 63.1 (t, C_{13}), 37.7 (d, C_6), 36.1 (t, C_5), 35.1 (t, C_3, C_{14}), 32.3 (t, C_8, C_{10}), and 22.7 (d, C_4).

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(26) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390.

(27) The structural formula of diamantane was chosen as the Emblem of the 19th IUPAC Congress in London in 1963 and called "congressane". The molecule was unknown at the time and the IUPAC committee had invited a synthesis as "a challenging objective for the participants in the congress". Diamantane was synthesized in 1965: Cupas, C.; Schleyer, P. v. R.; Trecker, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 917.

(28) (a) Gund, T. M.; Schleyer, P. v. R. *Tetrahedron Lett.* **1973**, 959. (b) Gund, T. M.; Schleyer, P. v. R.; Unruh, G. D.; Gleicher, G. J. *J. Org. Chem.* **1974**, *39*, 2995.

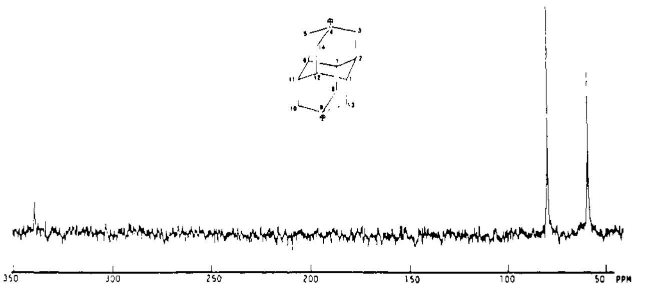
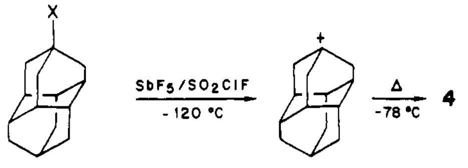


Figure 6. Proton-decoupled ^{13}C NMR spectrum (20 MHz) of 4,9-diamantyl cation **5** in SbF_5/SO_2ClF at -80 °C.

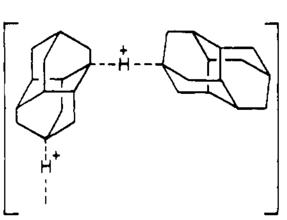
The 2D ^{13}C–^1H chemical shift correlation spectrum of 1-diamantyl cation in SbF_5/SO_2 is shown in Figure 5. From the correlation peaks in 2D NMR and the ^{13}C chemical shift assignment based on intensity and multiplicity data confirms our previous assignment of the ^1H resonances, particularly the assignment of the lowest field peaks to the γ-hydrogen resonance. Moreover, one can also assign the ^1H chemical shifts of all the proton within ±0.1 ppm accuracy (cf. Table I). The two protons attached to C_3 (as well as those to C_{14}, C_8, and C_{10}) are nonequivalent and as expected appear as a well-resolved AB quartet in the 2D spectrum, while they were unresolved multiplets centered at δ 2.03 in the ^1H NMR spectrum.

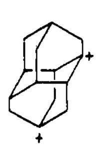
Before discussing the ^{13}C NMR chemical shift data, it is instructive to compare **4** with its apical bridgehead analogue, the 4-diamantyl cation **27**. The cation **27** was obtained by the



28-X (X: OH, F) **27**

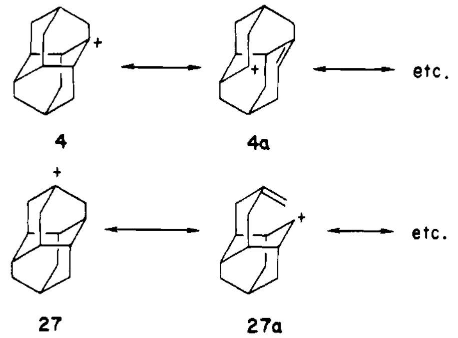
ionization of 4-diamantyl derivatives **28**-X in SbF_5/SO_2ClF at −120 °C. Ion **27** is, however, rather unstable and smoothly rearranges to **4** at −78 °C (half-life ~3.5 h). Consequently, it was impossible to obtain **27** devoid of traces of **4** even when the ionizations were carried out at −120 °C. This clearly indicates that the belt ion **4** is thermodynamically more stable than its apical isomer **27**. In fact, 4-diamantyl derivatives have been isomerized to 1-diamantyl derivatives by McKervey.[29] The rearrangement of **27** to **4** can be best rationalized by an intermolecular pathway rather than by intramolecular hydride shifts, similar to related rearrangements in the parent adamantane series. The fascile intermolecular rearrangement of **27** to **4** even at −78 °C is surprising considering that the transition state for such a process is rather hindered and may involve a 1,4-dicationic intermediate **29**.[28b]



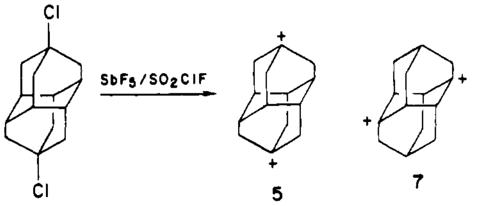


29

The ^{13}C NMR spectrum of **27** at −90 °C shows six absorptions at δ ^{13}C 305.1 (s), 91.7 (d), 63.7 (t), 37.6 (d), 30.9 (t), and 29.4 (d). The apical carbocationic center and the γ-bridgehead carbons (C_2, C_6, and C_{12}) are more deshielded (δ ^{13}C 305.1 and 91.7) compared to those in the 1-adamantyl cation **3a**. In contrast, the belt carbocationic center in **4** is more shielded at δ 297.9. This is exactly the opposite trend observed in diamantane (**2**)[31] (the apical carbon is more shielded than the belt carbon by 11.7 ppm). These differences can again be rationalized by a C–C hyperconjugative effect[15] in the cations. The mesomeric structure **4a** is more stabilized than **27a** due to substitution at the α position in the former.



4,9-Diamantyl Dication 5 and Attempted Preparation of 1,6-Diamantyl Dication 7. As shown earlier, all our attempts to generate the 1,3-adamantyl dication **8** were unsuccessful. The "single-cage" hydrocarbon cannot accommodate two positive charges at the bridgehead position. However, diamantane provides a much larger separation in its expanded cage. It is, therefore, possible to accommodate a formal positive charge in each of the two fused adamantane cages. Clearly isomer **5** ("apical–apical")



30 **5** **7**

should be the most stable since it would experience the least charge–charge repulsion. Apparently such charge repulsion would be maximum in the belt–belt isomer **7** and intermediate in apical–belt isomer **29**.

We have succeeded in preparing the 4,9-diamantyl dication **5** by the ionization of apical–apical 4,9-dichlorodiamantane (**30**) in SbF_5/SO_2ClF. The ^{13}C NMR spectrum of **5** in SbF_5/SO_2ClF at −80 °C (Figure 6) shows only three absorptions at δ ^{13}C 337.3 (s), 78.8 (d, J_{C-H} = 147.5 Hz), and 58.3 (t, J_{C-H} = 147.5 Hz). The high symmetry as well as the observation of highly deshielded carbocationic absorption clearly supports the formation of **5**. The bridgehead carbons (at C_1, C_2, C_7, C_6, C_{11}, and C_{12}) are rather shielded as compared to those in either **3a** or **27**. This shows that due to the presence of two positive charges centered at C_4 and C_9 positions, the hyperconjugative stabilization by the C_β–C_γ bond may not be as important. This is again reflected by the large deshielding of the cationic center δ ^{13}C 337.3 compared to δ ^{13}C 300 in **3a** and δ ^{13}C 305.1 in **27**.

Surprisingly when the ionization of **30** is carried out in SbF_5/SO_2 solution instead of SO_2ClF, a different ^{13}C NMR spectrum was obtained. Although three peaks are still observed at δ ^{13}C 230.9 (s), 64.7 (d), and 51.4 (t) which are assigned to the α, γ, and β carbons, respectively, C_α is highly shielded compared to that of **5** in SbF_5/SO_2ClF solution (by ca. 107 ppm). This indicates that the carbocationic center is significantly modified by complexation with more nucleophilic sulfur dioxide. This is the first example of the complexation of a tertiary carbocationic center by sulfur dioxide (although secondary and primary systems are known to interact). The observed dication in SO_2 is assigned the structure **31**.

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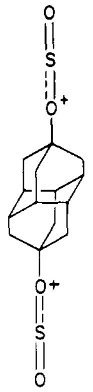
(29) Courtney, T.; Johnson, D. E.; McKervey, M. A.; Rooney, J. J. *J. Chem. Soc., Perkin Trans 1* **1972**, 2962.

(30) Schleyer, P. v. R.; Lam, L. K. M.; Raber, D. J.; Fry, J. L.; McKervey, M. A.; Alford, J. R.; Cuddy, B. D.; Keizer, V. G.; Geluk, H. W.; Schlatmann, J. L. M. A. *J. Am. Chem. Soc.* **1970**, *92*, 5246.

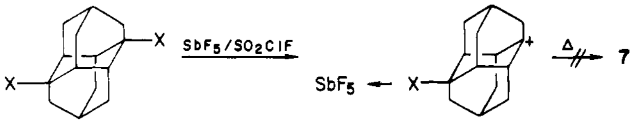
(31) Duddeck, H.; Hollowood, F.; Karim, A.; McKervey, M. A. *J. Chem. Soc., Perkin Trans 2* **1979**, 360.

The shielding of C_α (C_4 and C_9) carbons is again reflected by the relative shielding of β and γ carbons. Charge–charge repulsion in dication **5**, as discussed, diminshes charge delocalization into the σ framework by C–C hyperconjugation, thus localizing the charge at the carbocationic centers and rendering them more reactive toward SO_2.



31

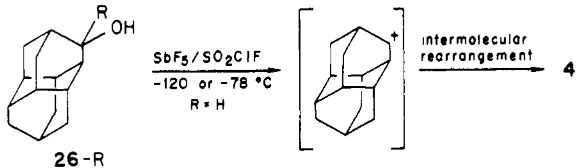
We also attempted to prepare the belt-belt isomeric 1,6-diamantyl dication **7** by the ionization of 1,6-dihalodiamantanes **32**-X (X = Br and F) in SbF_5/SO_2ClF and other superacids such as FSO_3H: SbF_5/SO_2ClF and HF/SbF_5 under various conditions. In all cases only the monocation monodonor–acceptor complex **33** was obtained, and the 1,6-dication **7** was not formed.



32-X (X: Br, F)

33

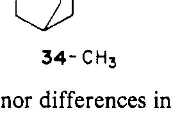
3-Diamantyl Cations. As mentioned before, dissolution of 3-diamantanol **26**-H in SbF_5/SO_2ClF either at −78 or −120 °C gives only the rearranged bridgehead 1-diamantyl cation **4**. No evidence was obtained for the intermediate secondary 3-diamantyl cation **34**. This rearrangement is similar to the rearrangement of the 2-adamantyl cation to **3a**.[8,9] The mechanism for such a rearrangement, considering the orientation of the orbitals involved, again probably occurs through an intermolecular rather than an intramolecular mechanism.[8,9]



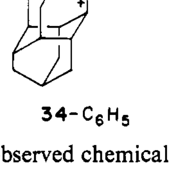
26-R
R: H, CH3, C6H5

34-H

On the other hand, dissolution of methyl-substituted **26**-CH_3 in SbF_5/SO_2ClF at −78 °C gave the 3-methyl-3-diamantyl cation **34**-CH_3, which was found to be stable up to room temperature without undergoing any rearrangement or decomposition. The ion **34**-CH_3 shows the following ^{13}C NMR absorptions: δ ^{13}C 312.4 (s), 73.5 (d), 59.3 (d), 53.7 (d), 47.5 (t), 37.9 (q), 34.5 (d), 34.2 (d), 33.9 (t), 32.7 (t), and 22.0 (d). The assignment of individual carbon atoms are shown in Table II. The cation **34**-CH_3 is comparable to 2-methyl-2-adamantyl cation,[8] although there are some minor differences in the observed chemical shifts of the former. The C_2 and C_4 carbon atoms which are α to the cationic center in **34**-CH_3 are deshielded to a different degree (C_2 at δ 73.5 and C_4 at δ 59.3). This is in accordance with deshielding trend observed in the parent hydrocarbon diamantane **2** (C_2 at δ 37.7 and C_4 at δ 26.0).[31]



34-CH3



34-C6H5

The 3-phenyl-3-diamantyl cation **34**-C_6H_5 was also obtained by the ionization of **26**-C_6H_5 in SbF_5:FSO_3H/SO_2ClF at −78 °C. Ion **34**-C_6H_5 is like any regular phenyl-substituted trivalent carbocation. The ^{13}C NMR spectrum of C_6H_5-**34** indicates extensive positive charge delocalization into the aryl ring (Table II). The para carbon is observed at δ ^{13}C 151.2 which is close to that observed in 2-phenyl-2-adamantyl cation[8] (δ 154.2). Again one observes that the C_2 and C_4 carbons are deshielded differently (difference of 13.2 ppm) similar to that in neutral diamantane (**2**) (difference of 11.7 ppm).

Conclusion

The bridgehead 1-adamantyl (**3a**), 3-methyl-1-adamantyl (**3b**), 3,5-dimethyl-1-adamantyl (**3c**), and 3,5,7-trimethyl-1-adamantyl (**3d**) cations were prepared in superacid medium and characterized by ^1H and ^{13}C NMR spectroscopy. The bridgehead 1- and 4-diamantyl cations **4** and **27** were also prepared and characterized by NMR spectroscopy. The 4-diamantyl cation **27** slowly and irreversibly rearranges to the more stable 1-diamantyl cation, **4**. Ionization of the secondary 2-adamantyl and 3-diamantyl derivatives gives the corresponding bridgehead tertiary cations **3a** and **4**, respectively. The above rearrangements to the thermodynamically more stable bridgehead cations has been rationalized in terms of facile intermolecular hydrogen shifts.

The solid-state ^{13}C NMR spectrum of 1-adamantyl cation **3a** (as its SbF_6^- salt) was also recorded. Except for some line broadening, the solid-state ^{13}C NMR spectrum is almost identical with the solution spectrum in SbF_5/SO_2ClF solution. The 2D ^{13}C–^1H chemical shift correlation spectra of 1-adamantyl and 1-diamantyl cations in SbF_5/SO_2 were also obtained. The correlation peaks were used to assign many NMR chemical shifts. The relative deshielding of bridgehead γ carbons (and protons) with respect to β-methylenes in the bridgehead cations has been rationalized in terms of C–C hyperconjugation effect. 3,3′-(1,1′-Biadamantyl) dication **6** and 4,9-diamantyl dication **7** were also generated and studied. The charge–charge repulsion in **7** seems to diminish C–C hyperconjugative interaction which is found to be "operative" in all other bridgehead cations including **6**. Attempts to prepare 1,3-adamantyl and 1,6-diamantyl dications were, however, unsuccessful.

The equilibrating 2,3-trimethylene-2-norbornyl cation **12** is formed from the ionization of *exo*-5,6-trimethylene-2-norbornyl derivatives. The barrier for the degenerate 2,3-hydrogen shift has been estimated to be 7.2 kcal/mol. While cation **12** is quite stable in SO_2ClF solution even at room temperature, in SO_2 it smoothly and irreversibly rearranges to 1-adamantyl cation **3a**.

Experimental Section

The 1- and 2-adamantyl derivatives such as (chloro, bromo, and hydroxy compounds) were commercially available compounds. The 1- and 2-fluoroadamantanes were prepared by using HF/pyridine reagent[32] from their corresponding hydroxy derivatives. 1-Bromo-3-methyl-, 1-bromo-3,5-dimethyl-, and 1-bromo-3,5,7-trimethyladamantanes were prepared by the bromination[33] of the corresponding methyladamantanes (purchased from Aldrich Chemicals). The *exo*-chloro-, bromo-, and hydroxy-*exo*-trimethylenenorbornanes **9**-X were prepared according to the literature methods.[34,35] 2-Methyl-2-*endo*-hydroxy-5,6-*exo*-trimethylenenorbornane (**16**) (mp 78.5–79.5 °C) was prepared from 2-trimethylenenorbornanone[35] and methylmagnesium iodide in diethyl ether. 1,1′-Biadamantane (**21**) and 3,3′-dibromo-1,1′-biadamantane (**22**) were prepared from adamantane (**1**).[36] 1,3-Difluoroadamantane (**23**)[27]

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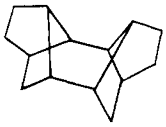
was prepared from the readily available 1,3-dibromoadamantane.[38]

Diamantane (**2**) was prepared by the literature procedure[39,40] starting from the commercially available norbornadiene in three steps. The 1-diamantyl compounds **25**-X (X = Cl and OH) and 4-diamantyl derivatives **28**-X (X = Cl and OH) were prepared from diamantane.[40] The fluoro compounds **25**-F and **28**-F were synthesized from the corresponding bromo compounds[28] by using the modified Ritter-type reaction in HF/pyridine medium.[41,42] The 4,9-dichlorodiamantane (**30**) was obtained by the chlorination of tetrahydrobinor-S in $ClSO_3H$.[43] (One of the referees questioned the structure of tetrahydrobinor-S. Tetrahydrobinor-S is a $C_{14}H_{20}$ hydrocarbon, whose exact structure[45] to date has not been determined. However, the two structures **35** and **36** have been proposed[46] based on the observation of seven ^{13}C resonances.



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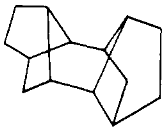

36

To answer the question, we have carried out carbon–carbon connectivity studies by using C–C–C 2D[47] NMR experiment and found the structure to be **36** and not **35**.[48] 1,6-Difluorodiamantane **32**-F was synthesized from 1,6-dibromodiamantane **32**-Br.[28] 3-Diamantanone and 3-hydroxydiamantane **26**-H and **26**-CH_3 are known compounds.[44,45] The phenyl-substituted analogue **26**-C_6H_5 was prepared by the addition of corresponding organo lithium compounds to 3-diamantanone in ether (**26**-C_6H_5, mp 111–112 °C). The new compounds **16** and **26**-C_6H_5, gave satisfactory spectroscopic and analytical data.

Preparation of Carbocations and Carbodications. Freshly distilled SbF_5 and FSO_3H were used. To appropriate superacid dissolved in twofold excess amount of SO_2ClF or SO_2 at dry ice–acetone temperature (−78 °C) or ethanol–liquid N_2 slush (~−130 °C) was slowly added with vigorous stirring a cooled slurry or solution of the appropriate precursor in SO_2ClF or SO_2, resulting in an approximately 10–15% solution of the cation or dication. The quenching experiment to obtain alcohol **11** was carried out by pouring the ion solution over crushed ice with rapid stirring. The aqueous layer was neutralized with solid $NaHCO_3$ and extracted with ether which upon evaporation gave **11**.

^1H NMR spectra were obtained either on a 60-MHz Varian A 56/60, 100-MHz Varian XL-100, or 200-MHz Varian XL-200 NMR spectrometers equipped with low-temperature probes. The 250-MHz spectra were recorded at Carnegie-Mellon University with an instrument equipped with a superconducting solenoid with a magnetic field of 58.7 kG.

^{13}C NMR spectra were obtained on Varian Models, FT-80, XL-100, and XL-200 NMR spectrometers equipped with a low-temperature broad-band probe.

All the ^1H and ^{13}C NMR chemical shifts are referenced from external capillary tetramethylsilane.

Heteronuclear correlated 2D NMR spectra were recorded on a Varian XL-200 NMR spectrometer equipped with Nicolet Zeta-8 Model plotter at 50-MHz ^{13}C resonance frequency. The pulse sequence used[16] is $90°(H) - (t_1)/2 - 180°(C) - (t_1)/2 - \tau_1 - 90°(H)\ 90°(C) - \tau_2 - FID(t_2)$, where t_1 is the evolution period and t_2 is the detection period during which broad-band ^1H decoupling was performed. The experiment was performed in quadrature in both the proton and carbon dimensions, and the data were obtained by using a 4000-Hz spectral width for carbon and 1000-Hz spectral width for proton. For adamantyl cation 16, transients were collected for each of 256 different values of the evolution period, and for the diamantyl cation 64 transients were collected for each of 128 different values of the evolution period. A Föurier number of 1K was used for transformation in both domain. Figures 3 and 5 show both the stacked plots and the contour plots. Chemical shifts were measured from the individual traces of the correlation peaks.

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Registry No. 2, 2292-79-7; **3a**, 19740-18-2; **3a**·SbF_6^-, 2062-52-4; **3b**, 72235-81-5; **3c**, 95531-29-6; **3d**, 95531-30-9; **4**, 95531-33-2; **5**, 95531-36-5; **6**, 95531-32-1; **7**, 95531-43-4; **8**, 95531-44-5; **9**, 26378-05-2; **11**, 86594-77-6; **12**, 95531-31-0; **16**, 27292-76-8; **17**, 95531-34-3; **21**, 3732-31-8; **22**, 15417-11-5; **23**, 54043-61-7; Br-**25**, 30545-17-6; Cl-**25**, 32401-16-4; HO-**25**, 30545-19-8; F-**25**, 77052-09-6; CH_3-**26**, 30545-26-7; C_6H_5-**26**, 95531-42-3; H-**26**, 30545-24-5; **27**, 95531-35-4; Br-**28**, 30545-30-3; Cl-**28**, 32401-17-5; F-**28**, 77052-10-9; HO-**28**, 30651-03-7; **30**, 32401-20-0; **31**, 95531-37-6; Br-**32**, 32401-10-8; F-**32**, 90481-60-0; F-**33**, 95531-38-7; H-**34**, 95531-45-6; CH_3-**34**, 95531-39-8; C_6H_5-**34**, 95531-40-1; **36**, 51966-18-8; SbF_5, 7783-70-2; norbornadiene, 121-46-0; 3-diamantanone, 30545-23-4; 2-*exo*-chloro-5,6-*exo*-trimethylenenorbornane, 56914-94-4; 1-fluoroadamantane, 768-92-3.

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