

## Investigations on intriguing long lived carbocations

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**Abstract:** Triaxane-2-methyl alcohol and ditriaxane-2,10-dimethyl alcohol upon ionization in superacids gave mono and dication species which can be characterized as nonclassical bicyclobutonium type cations. Polycyclic [1.1.1.1]- and [2.2.1.1]isopagodanes undergo two electron oxidation to respective 4c/2e  $\sigma$ -bishomoaromatic cyclobutane dication species in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution at  $-78^\circ\text{C}$ . These intriguing dication species were characterized by low temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy as well as theoretical calculations. Mesityl-2,6-dimethyldiyl dication was also prepared by the ionization of 2,6-bis(chloromethyl)mesitylene in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ . Its structure compared with the elusive benzene dication. Related dienyl and allylic dication species were also characterized under long lived stable ion conditions.

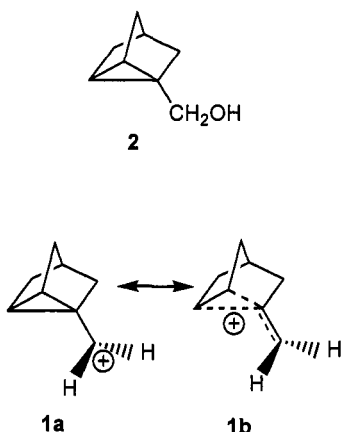
In the past two decades the study of long lived carbocations has been of considerable interest (1). Previous studies on carbocations have shown that in the absence of aryl stabilization of the carbocation centers, persistent (long lived) dipositive ions can be generated only if the carbocation centers are separated by at least two carbon atoms and the carbenium centers are tertiary (1,2). On the other hand, if the carbocationic centers can be stabilized by allyl conjugation or aromatic stabilization, carbocations can be generated wherein the positively charged centers can be more proximal. In this account we describe some recent studies on long lived distal as well as proximal carbocations with some unusual bonding and charge stabilization characteristics. The study includes not only NMR characterization but also theoretical studies and NMR chemical shift calculations.

### Triaxane-2-methyl Cation and Ditriaxane-2,10-dimethyldiyl Dication

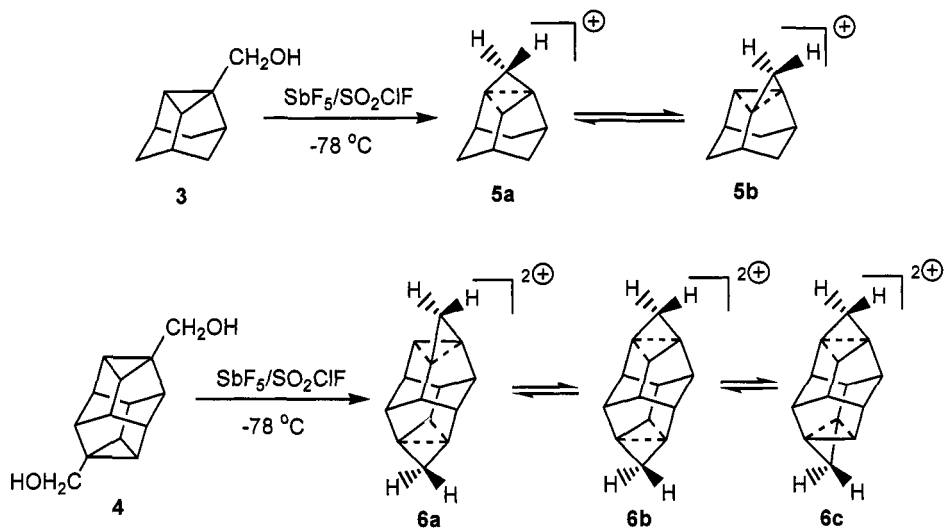
Cyclopropylmethyl cations are among the most extensively studied class of carbocations. The rapid interconversion of cyclopropylmethyl, cyclobutyl, and homoallyl derivatives in carbocationic reactions has attracted considerable attention. Historically cyclopropylmethyl cations were the first carbocations to be named "nonclassical" and many interesting and intriguing studies concerning the direct observation of cyclopropylmethyl cations under stable ion conditions by NMR spectroscopy have been recently reviewed (3). The parent primary cyclopropylmethyl cation  $\text{C}_4\text{H}_7^+$  was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy under stable ion conditions by Olah and co-workers as early as 1970 (4). Subsequent low temperature NMR evidence from  $^{13}\text{C}$  (5,6) and  $^2\text{H}$  labeled (7) systems including solid state NMR measurements (8a) and high level *ab initio* calculations (8b) excluded classical cyclopropylmethyl or cyclobutyl ion structures. The cyclopropylmethyl cation has been shown to be a rapidly equilibrating mixture of nonclassical bicyclobutonium cations and the bisected cyclopropylmethyl cation (6,7,8).

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The only known example of a "static" bisected primary cyclopropylmethyl cation **1** was prepared by Schmitz and Sorensen by ionizing nortricyclane-1-methanol **2** with  $\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  at low temperature (9). In **2** the cyclopropyl moiety is locked in a norbornane framework.

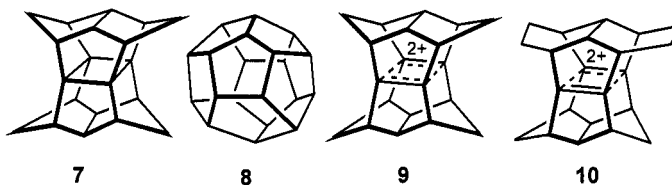


In the cyclopropylmethyl alcohol derivatives, triaxane-2-methyl alcohol **3** (10a) and ditriaxane-2,10-dimethyl alcohol **4** (10b), the cyclopropyl moieties are also locked into rigid hydrocarbon frameworks. As potential precursors to related cyclopropylmethyl cations, we have explored the behavior of **3** and **4** under stable ion conditions. The observed intriguing mono and dication were characterized by low temperature  $^{13}\text{C}$  NMR spectroscopy. Ion generated from alcohol **3** was deduced to be a set of rapidly equilibrating bicyclobutonium ions **5**. Similar conclusions were made for the intriguing dication **6** generated from diol **4**. IGLO calculations on Density functional theory (DFT) optimized structures helped resolve the nature of the monocation **5** (11).



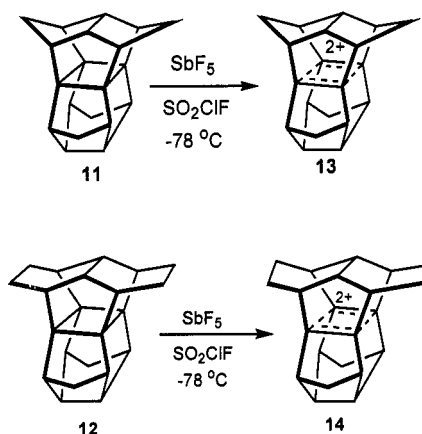
**Polycyclic [1.1.1.1] and [2.2.1.1]Isopagodvl Dications**

Synthesis of  $C_{20}H_{20}$  molecule named [1.1.1.1] pagodane ( $D_{2h}$  symmetry) **7** has received considerable attention due to its close isomeric relationship to highly symmetrical ( $I_h$ ) pentagonal dodecahedrane **8** (12). In fact, [1.1.1.1] pagodane derivatives have been transformed to pentagonal dodecahedrane skeleton in high yield (12).



An other interesting aspect of the pagodane structure is the presence of a planar cyclobutane ring. In our previous work we were able to smoothly oxidize the planar highly strained rectangular cyclobutane ring in [1.1.1.1] and [2.2.1.1] pagodanes to their respective dications **9** and **10** under long lived stable ion conditions and characterized them by  $^1H$  and  $^{13}C$  NMR spectroscopy (13). These dications **9** and **10** were also recognized as two-electron stable frozen Woodward-Hoffmann transition state analogs (13). The stability of these intriguing dications was also rationalized by ab initio/IGLO theoretical calculations (14).

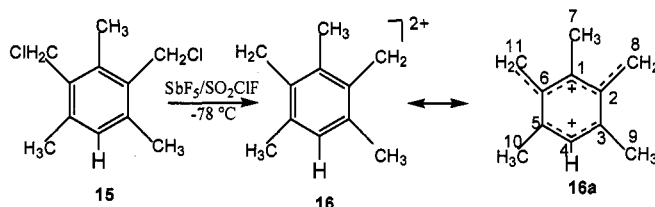
More recently isomeric highly symmetric [1.1.1.1]isopagodane **11** and its bishomo analog [2.2.1.1]isopagodane **12** were also synthesized (15) in order to explore the unusual cage radical cations and dications. Even though the interaction of ethylene and ethylene radical cation to form cyclobutane radical cation is symmetry forbidden, such a  $4c/3e$  radical cation was found stabilized in the rigid [1.1.1.1]pagodane and [1.1.1.1]isopagodane skeletal frame-works (16a,b). On the other hand, interaction of ethylene and ethylene dication is symmetry allowed based on Woodward-Hoffmann theory (13,14). Smooth two-electron oxidation of both [1.1.1.1]isopagodane **11** and [2.2.1.1]isopagodane **12** in  $SbF_5/SO_2ClF$  solutions to their respective diamagnetic dications, **13** and **14**, takes place at  $-78^\circ C$  through the intermediacy of respective mono radical cations. Their characterization was achieved by low temperature  $^1H$  and  $^{13}C$  NMR spectroscopy (17).



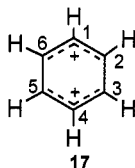
The structures of the intriguing dications **8** and **10** were also computed by DFT calculations. The  $^{13}C$  NMR chemical shifts were calculated using both GIAO and IGLO methods. Both dications **8** and **10** can also be characterized as  $4c/2e$   $\sigma$ -bishomoaromatic rectangular cyclobutane dications as well as frozen Woodward-Hoffmann transition state analogs (17).

### Mesityl-2,6-dimethyldiyl Dication and Related Dienylic and Allylic Dication Analogs

Ionization of 2,6-bis(chloromethyl)mesitylene **15** in five-fold excess of  $\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$  resulted in a deep red colored solution (**18**). The 75 MHz  $^{13}\text{C}$  NMR spectrum exhibited seven well-resolved peaks at  $\delta^{13}\text{C}$  218.5 (s), 198.2 (t,  $J_{\text{C,H}}=170.3$  Hz) 195.4 (s), 143.9 (s), 140.0 (d,  $J_{\text{C,H}}=177.3$  Hz), 25.6 (q,  $J_{\text{C,H}}=131.9$  Hz), 23.9(q,  $J_{\text{C,H}}=132.3$  Hz). The 300-MHz  $^1\text{H}$  NMR showed absorptions at  $\delta^1\text{H}$  8.77 (br, 2H), 8.51 (br, 2H), 7.10 (singlet, 1H), 2.62 (singlet, 3H) and 2.10 (singlet, 6H). The ion is remarkably stable even at  $-10^\circ\text{C}$ . Based on the observed NMR data a dienylic allylic dication system **16a** appears to be the major contributor to the structure **16**. The remarkable stability of the dication can be attributed to highly stabilized dienylyl-allyl dication nature (i.e. **16a**).



Dicationic structure **16a** is reminiscent of the bisallylic benzene dication **17**. The benzene dication **17** is experimentally still elusive although di and polycyclic analogs were obtained by two-electron oxidation of the corresponding arenes by  $\text{SbF}_5$  (**19**). MINDO/3 calculations by Dewar et al. (**20a**) showed that the benzene dication **17** favors a  $\text{C}_{2h}$  chair conformation as the most stable form, with essentially isolated allyl cation units. Schleyer et al. subsequently found (**20b**) that **17** is subject to Jahn-Teller distortion upon optimization forming a double allylic cation. According to Schleyer et al. (**20c**), the uncoupling of the allyl units in **17** tends to keep the pairs of  $\pi$ -electrons as far apart from one another as possible, thus minimizing the repulsions between them. This leads to unequal bond lengths in the ring and forces the ring to be distorted from planarity.

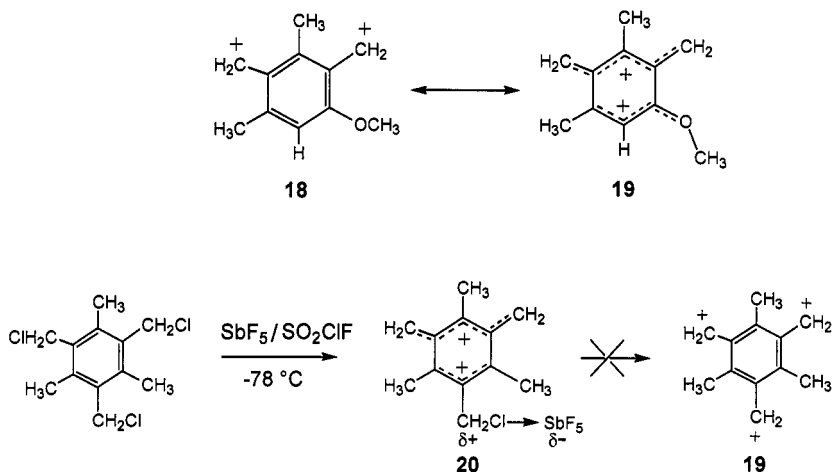


The predominant resonance contribution of **16a** was also indicated by density functional theory (DFT)/IGLO calculations. The geometry was fully optimized at the DFT B3LYP/6-31G\* level. The  $\text{C}_s$  symmetrical structure **16a** is the global minimum for the dication on the potential energy surface.  $\text{C}_6\text{-C}_{11}$  bond distance is 1.377 Å, slightly longer than that of a double bond (1.34 Å). On the other hand,  $\text{C}_1\text{-C}_2$  bond distance is 1.451 Å, between those of single (1.54 Å) and double bond. Thus, one of the positive charges of the dication is asymmetrically delocalized over the  $\text{C}_8\text{-C}_2\text{-C}_1\text{-C}_6\text{-C}_{11}$  atoms (i.e. dienylyl cation). The other positive charge is delocalized among  $\text{C}_5\text{-C}_4\text{-C}_3$  atoms (i.e. allyl cation) as the bond distance of  $\text{C}_3\text{-C}_4$  (1.393 Å) is between those of single and double bond. So, the dication **16a** can be described as dienylyl-allyl dication.

The structure can also be considered as a substituted benzene dication. **16a** is slightly distorted from its planarity as the  $\text{C}_1\text{-C}_2\text{-C}_3\text{-C}_4$  dihedral angle was found to be  $3.0^\circ$ . There seems to be very little interaction between dienylyl and allyl part of the dication as the  $\text{C}_2\text{-C}_3$  bond distance (1.474 Å) is close to that of a single bond.

charges. The bond orders of C<sub>6</sub>-C<sub>11</sub> and C<sub>1</sub>-C<sub>6</sub> are 1.63 and 1.23, respectively, and the atomic charge of C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> are +0.32, -0.19 and -0.02 a.u. is again indicating asymmetrical charge delocalization over C<sub>8</sub>-C<sub>2</sub>-C<sub>1</sub>-C<sub>6</sub>-C<sub>11</sub> atoms. C<sub>2</sub>-C<sub>3</sub> bond order of 1.13, indicating only little interaction between dienylic and allylic part of the dication. IGLO calculated <sup>13</sup>C NMR chemical shifts of **16a** also correlate very well with the experimentally obtained data (21).

Similarly, 2,6-dimethyl-5-methoxy-m-xilyldiyl dication **18** can be considered as dienylic and methoxy stabilized allylic dication **18a**. Attempted preparation of 2,4,6-trimethylmesityryl trication **19** starting from 2,4,6-tris(chloromethyl)mesitylene instead led to the dication **20** (21).



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### References

- 1 G. K. S. Prakash, T. N. Rawdah, G. A. Olah. *Angew. Chem., Int. Ed. Engl.* **22**, 390 (1983).
- 2 G. K. S. Prakash, P. v. R. Schleyer (Eds.). *Stable Carbocation Chemistry*, Wiley Interscience, New York (1997) and references cited therein.
- 3 G. A. Olah, V. P. Reddy, G. K. S. Prakash. *Chem. Rev.* **92**, 69 (1992).
- 4 G. A. Olah, D. P. Kelly, C. L. Juell, R. D. Porter. *J. Am. Chem. Soc.* **92**, 2544 (1970).
- 5 (a) G. A. Olah, C. L. Juell, D. P. Kelly, R. D. Porter. *J. Am. Chem. Soc.* **94**, 146 (1972);  
(b) J. Staral, I. Yavari, J. D. Roberts, G. K. S. Prakash, D. J. Donovan, G. A. Olah. *J. Am. Chem. Soc.* **100**, 8016 (1978).
- 6 (a) W. J. Brittain, M. E. Squillacote, J. D. Roberts. *J. Am. Chem. Soc.* **106**, 7280 (1984);  
(b) M. Saunders, K. E. Laidig, M. Wolfsberg. *J. Am. Chem. Soc.* **111**, 8989 (1989).
- 7 M. Saunders, H.-U. Siehl. *J. Am. Chem. Soc.* **102**, 6868 (1980).
- 8 (a) P. C. Myhre, G. G. Webb, C. S. Yannoni. *J. Am. Chem. Soc.* **112**, 8992 (1990);  
(b) M. Saunders, K. E. Laidig, K. B. Wiberg, P. v. R. Schleyer. *J. Am. Chem. Soc.* **110**, 7652 (1988) and references cited therein.
- 9 T. S. Sorensen, L. R. Schmitz. *J. Am. Chem. Soc.* **104**, 2600 (1982).

- 10 (a) Alcohol **3** was prepared in 59 % yield by the reduction of triaxane-2- carboxylic acid with lithium aluminum hydride.  
(b) 2,10-(*p*-[3<sup>2</sup>.5<sup>6</sup>]Octahedrane)dimethanol **4** was obtained in 74 % yield by the reduction of 2,10-(*p*-[3<sup>2</sup>.5<sup>6</sup>]octahedrane)-dicarboxylic acid dimethylester with lithium aluminum hydride; Ch.-H. Lee, S. Liang, T. Haumann, R. Boese, A. de Meijere. *Angew. Chem. Int. Ed. Engl.* **32**, 559 (1993).
- 11 G. A. Olah, H. A. Buchholz, G. K. S. Prakash, G. Rasul, J. J. Sosnowski, R. K. Murray Jr., M. A. Kusnetsov, S. Liang, A.de Meijere. *Angew. Chem. Int. Ed. Engl.* **35**, 1499 (1996)
- 12 For a comprehensive review see H. Prinzbach, K.Weber. *Angew. Chem. Int. Ed. Engl.* **33**, 2239 (1994) and references cited therein.
- 13 G. K. S. Prakash, V. V. Krishnamurthy, R. Herges, R. Bau, H. Yuan, G. A. Olah, W-D. Fessner, H. Prinzbach. *J. Am. Chem. Soc.*, **108**, 836 (1986); *J. Am. Chem. Soc.* **110**, 7764 (1988).
- 14 R. Herges, P. v. R. Schleyer, M. Schindler, W-D. Fessner. *J. Am. Chem. Soc.*, **113**, 3649 (1991).
- 15 M. Wollenweber, R. Pinkos, J. Leonhardt, H. Prinzbach. *Angew. Chem. Int. Ed. Engl.* **33**, 117 (1994).
- 16 (a) K. Weber, G. Lutz, L. Knothe, J. Mortensen, J. Heinze, H. Prinzbach. *J. Chem. Soc. Perkin Trans. 2.*, 1991 (1995).  
(b) H. Prinzbach, M. Wollenweber, R. Herges, H. Neumann, G. Gescheidt, R. Schmidlin. *J. Am. Chem. Soc.* **117**, 1439 (1995).
- 17 G. K. S. Prakash, K. Weber, G. A. Olah, H. Prinzbach, M. Wollenweber, M. Etkorn, T. Voss, R. Herges, unpublished results.
- 18 The dication **16** was prepared by careful addition of the precursor **15** (~30 mg) to well-stirred 1.5 mL of a 50% v/v solution of SbF<sub>5</sub> in SO<sub>2</sub>ClF at -78 °C.
- 19 (a) G. A. Olah, D. Forsyth. *J. Am. Chem. Soc.* **98**, 4086 (1976);  
(b) G. A. Olah, B. P. Singh. *J. Org. Chem.* **48**, 4830 (1983).
- 20 (a) M. J. S. Dewar, M. K. Holloway. *J. Am. Chem. Soc.* **106**, 6619 (1984);  
(b) P.v. R. Schleyer, K. Lammertsma. *J. Am. Chem. Soc.* **105**, 1049 (1983);  
(c) P. v. R. Schleyer, K. Lammertsma, H. Schwarz. *Angew. Chem. Int. Ed. Engl.* **28**, 1321 (1989).
- 21 G. A. Olah, T. Shamma, A. Burrichter, G. Rasul, G. K. S. Prakash, *J. Am. Chem. Soc.* **119**, 12923 (1997).