Investigations on intriguing long lived carbodications

G. K. Surya Prakash

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, USA

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

In the past two decades the study of long lived carbodications has been of considerable interest (1). Previous studies on carbodications have shown that in the absence of aryl stabilization of the carboxation centers, persistent (long lived) dipositive ions can be generated only if the carboxation centers are separated by at least two carbon atoms and the carbenium centers are tertiary (1,2). On the other hand, if the carboxacion centers can be stabilized by allyl conjugation or aromatic stabilization, carbodications 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 carbodications 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-dimethylidivl 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 C$_4$H$_7^+$ was characterized by $^1$H and $^{13}$C NMR spectroscopy under stable ion conditions by Olah and co-workers as early as 1970 (4). Subsequent low temperature NMR evidence from $^{13}$C (5,6) and $^2$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 bicylobutonium cations and the bisected cyclopropylmethyl cation (6,7,8).
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 SbF₅ in SO₂ClF 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 dications were characterized by low temperature ¹³C 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).
Poly cyclic [1.1.1.1] and [2.2.1.1] Isopagodyl 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 $^1$H 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$_2$ClF solutions to their respective diamagnetic dications, 13 and 14, takes place at -78 °C through the intermediacy of respective mono radical cations. Their characterization was achieved by low temperature $^1$H 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 SbF5 in SO2ClF at -78 °C resulted in a deep red colored solution (18). The 75 MHz 13C NMR spectrum exhibited seven well-resolved peaks at δ13C 218.5 (s), 198.2 (t, Jc,H=170.3 Hz) 195.4 (s), 143.9 (s), 140.0 (d, Jc,H=177.3 Hz), 25.6 (q, Jc,H=131.9 Hz), 23.9(q, Jc,H=132.3 Hz). The 300-MHz 1H NMR showed absorptions at δ1H 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 °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 dienyl-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 SbF5 (19). MINDO/3 calculations by Dewar et al. (20a) showed that the benzene dication 17 favors a C2h 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 π-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 C8 symmetrical structure 16a is the global minimum for the dication on the potential energy surface. C6-C11 bond distance is 1.377 Å, slightly longer than that of a double bond (1.34 Å). On the other hand, C1-C2 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 C8-C2-C1-C6-C11 atoms (i.e. dienyl cation). The other positive charge is delocalized among C5-C4-C3 atoms (i.e. allyl cation) as the bond distance of C3-C4 (1.393 Å) is between those of single and double bond. So, the dication 16a can be described as dienyl-allyl dication.

The structure can also be considered as a substituted benzene dication. 16a is slightly distorted from its planarity as the C1-C2-C3-C4 dihedral angle was found to be 3.0°. There seems to be very little interaction between dienyl and allyl part of the dication as the C2-C3 bond distance (1.474 Å) is close to that of a single bond.
Intriguing long lived carbodication charges. The bond orders of C6-C11 and C1-C6 are 1.63 and 1.23, respectively, and the atomic charge of C1, C2 and C3 are +0.32, -0.19 and -0.02 a.u. is again indicating asymmetrical charge delocalization over C8-C2-C1-C6-C11 atoms. C2-C3 bond order of 1.13, indicating only little interaction between dienyl and allyl part of the dication. IGLO calculated $^{13}$C NMR chemical shifts of 16a also correlate very well with the experimentally obtained data (21).

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

![Diagram](image)

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References


(a) Alcohol 3 was prepared in 59% yield by the reduction of triaxane-2-carboxylic acid with lithium aluminum hydride.
(b) 2,10-(p-[32P]-Octahedral)dimethanol 4 was obtained in 74% yield by the reduction of 2,10-(p-[32P]-Octahedral)-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).


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 SbF5 in SO2ClF at -78 °C.

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