

## Exact structures of carbocations established by combined computational and experimental methods

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**Abstract:** The accuracy of *ab initio* geometries at various theoretical levels has been verified by comparing computed NMR chemical shifts and vibrational frequencies with the experimental spectra. Favorable comparisons are now made with Laube's X-ray structures of several nonclassical carbocations.

Significant chemical problems are reexamined periodically when new investigational methods become available. The first information concerning bonding and the structure of carbocations was inferred rather indirectly, e.g. from solvolysis rates and products. More details were revealed when it became possible, through G. Olah and his associates, to examine stable carbocations in superacid media.(1) However, only tertiary and a few secondary carbocations are directly observable e.g. by NMR spectroscopy. Important, but still only general features could be deduced concerning structures and bonding. Gas phase ion investigations provide energies, but geometries, e.g. of  $\text{CH}_3^+$  and  $\text{C}_2\text{H}_3^+$ , have only become available *experimentally* recently. Relatively few crystal structures of stable carbocations are available, but a series of interesting examples are now being reported by T. Laube.(2) These experimental advances are exciting, but progress is slow.

In contrast, theoretical calculations on carbocations at increasingly sophisticated and perhaps even definitive *ab initio* levels can now be carried out routinely. Not only stable species, but also short-lived intermediates with small activation barriers towards rearrangement and even transition structures can be examined with equal facility. This now provides a wealth of information to augment, extend, and help interpret experimental observations.

However, it is necessary to establish the "confidence limits" of the various computational levels which can be employed. Since carbocations were first examined theoretically a quarter century ago, quantum mechanics methods have improved dramatically. These developments, applied to carbocation problems, often have led to significant changes, e.g. in the relative energies of classical and nonclassical ions. The flat potential energy surfaces of many carbocations - low barriers and small energies between isomeric structures - offer continuing challenges for the computational chemist (as well as the experimentalist). How can we be sure that the levels of theory now employed are reliable and accurate? Is it possible that further, future developments of theory will give different results? Does solvation have an effect? To what extent do the computed equilibrium structures reflect those in solution or in the solid state?

A wealth of experience, including many extensive evaluations of the performance of various higher levels of *ab initio* theory, is now available.(3) The most sophisticated methods achieve "experimental accuracy", i.e. within the errors limits of the most precise experimental measurements. The gas phase energies of carbocations, which are not known to high accuracy, are reproduced quite satisfactorily by theory. But what about the geometries? The length of the partial bonds associated with nonclassical carbocations are of particular interest, since the distances and angles of the more conventional bonds are well reproduced at even modest levels of theory.

We have been obtaining answers to these questions by comparing computed with the available experimental data:(4) NMR chemical shifts, vibrational spectra, and X-ray structures. Accurately computed spectra allow the details of structures in super acid media to be deduced, e.g. by comparing vibrational frequencies as well as the IGLO(5, 6) and, still better, the GIAO-MP2(7)  $^{13}\text{C}$ -chemical shifts for various geometries with the experimental results. The bibliography(4) provides references to our papers, which cite other work in the area.

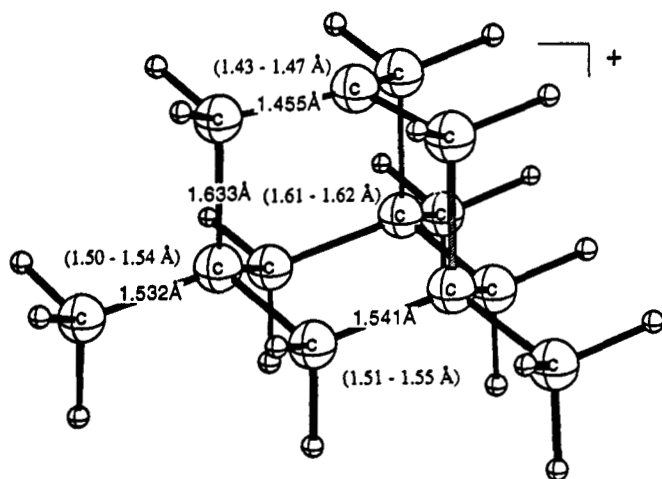
#### NMR Chemical Shifts.

W. Kutzelnigg's IGLO(5) was the first practicable program for the *ab initio* computation of chemical shifts. His associate, M. Schindler, first applied IGLO computations to carbocations,(6) but with mixed success. Our contribution was to show that most of the errors were due to the use of assumed or inadequate geometries. In contrast, structures optimized at e.g. MP2/6-31G\* led to good or excellent agreement with experiment. Still better results were achieved more recently by applying J. Gauss's GIAO-MP2 method,(7) which computes chemical shifts with inclusion of electron correlation. In particular, the results for unsaturated carbocations are improved greatly.(4w, y, bb)

Electron deficient carboranes and boranes afford the nearest neutral-molecule analogies for nonclassical carbocations, and have the advantage that many "accurate" structures have been determined by M.W., GED, and X-ray spectroscopy. Detailed evaluation of this data, via the degree of agreement between experimental and computed boron chemical shifts, revealed that MP2/6-31G\* geometries were generally more accurate and reliable than those which had been obtained experimentally.(8) The agreement between computed and experimental  $^{11}\text{B}$  chemical shifts is within 2 ppm over the entire 200 ppm experimental range. The *ab initio*/IGLO or GIAO/NMR method is now well established for structural determinations. The success with boron compounds provides additional confidence concerning the accuracy of geometries computed at MP2/6-31G\* or higher levels for carbocations.

#### Infrared Spectroscopy.

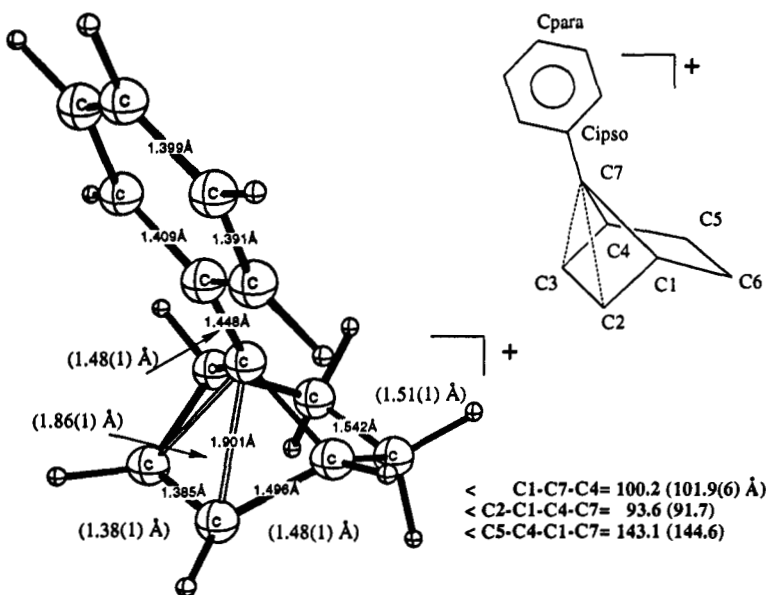
IR spectra were reported by Olah many years ago,(9) but Vancik and Sunko's recent development of cryogenic  $\text{SbF}_5$  matrix techniques(10) has enabled refined vibrational spectra of many carbocations to be determined. These are best interpreted by comparison with the vibrational frequencies computed *ab initio*, at MP2/6-31G\* or better levels. The shift in CH stretching vibrations to lower frequencies gave direct evidence for hyperconjugation, e.g. in the cyclopentyl(4g) and the isopropyl cation.(4b, h, p) An IR signal in the unusual  $2000\text{ cm}^{-1}$  region reveals the H-bridged structure of the 2-butyl(4i, j, u) and cyclooctyl cations.(4k) Our contributions in this area, many in collaboration with the Zagreb group, also are listed in the bibliography.



**Fig. 1.** 3,5,7-Trimethyl-1-adamantyl cation. Experiment: X-ray: reference (2a), values in parentheses. Ab Initio: Geometry: Becke3LYP/6-31G\*.

### X-ray Structures.

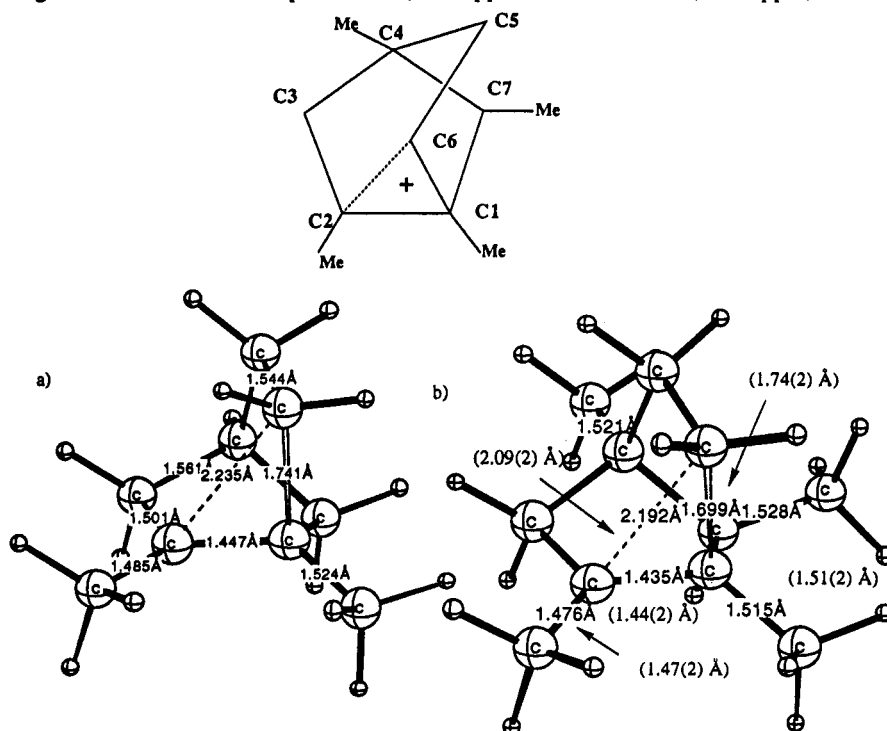
Early X-ray structures of carbocation salts were limited largely to aryl derivatives and aromatic systems. Recently, the continuing series of beautiful carbocation structures determined by Thomas Laube and his co-workers,(2) have inspired us to make direct comparisons with computed geometries, see Figs. 1 - 4. Unfortunately, it is often very difficult to obtain crystals of carbocation salts suitable for X-ray determination. The norbornyl cation, for example, gives highly crystalline but disordered salts. Consequently, Laube's structures do not deal with the parent of a given system, but are derivatives with methyl and other groups. Nevertheless, even such larger systems can now also be computed ab initio. The examples in Figs. 1 - 4 provide a progress report on our current results.



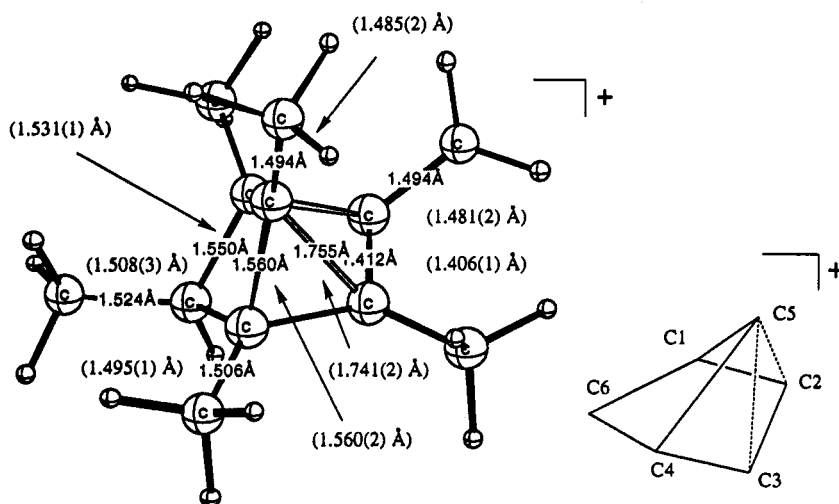
$\delta^{13}\text{C}$  NMR in ppm: C1/4: 43.9 [51.9]; C2/3: 144.6 [140.1]; C5/6: 19.4 [23.3];  
 C7: 108.6 [109.8];  $C_{\text{ipso}}$ : 113.3 [120.2];  $C_{\text{para}}$ : 147.2 [135.4]

**Fig. 2.** 2-Norbornen-7-yl cations. Experiment: X-ray ((*deloc*)-2,3-dimethyl-7-Ph-2-norbornen-7-yl cation): reference (2b), values in parentheses.  $\delta^{13}\text{C}$  (7-Ph-2-norbornen-7-yl cation): Olah, G. A.; Liang, G. J. *Am. Chem. Soc.* **97**, 6803 (1975), values in brackets. Ab Initio: geometry (7-Ph-2-norbornen-7-yl cation): MP2-FC/6-31G\*.  $\delta^{13}\text{C}$  (7-Ph-2-norbornen-7-yl cation): IGLO/DZ/MP2-FC/6-31G\*.

Figure 2 shows the optimized structure of the 7-Phenyl-7-norbornadienyl cation and also compares experimentally observed and computed  $^{13}\text{C}$  NMR chemical shifts. The X-ray structure has been determined for the 2,3-dimethyl-7-Ph-7-norbornadienyl cation, where the phenyl group has been found to be twisted out of the C1-C7-C4 plane by  $13^\circ$ , resulting in a C2-C7 bond length of 1.861 Å. (2b) In contrast, the phenyl group in the 7-Ph-7-norbornadienyl cation is parallel to the C2-C3 bond. Note the excellent agreement between the experimental (109.8 ppm) and theoretical (108.6 ppm) NMR signal for C7.



**Fig. 3.** 1,2-Dimethyl-2-norbornyl Cations. Experiment: b) X-ray (1,2,4,7-anti-tetramethyl-2-norbornyl cation): reference (2c), values in parentheses. Ab Initio: geometry: a) 1,2-Dimethyl-2-norbornyl cation: BeckeLYP/6-31G\*; b) 1,2,4,7-anti-tetramethyl-2-norbornyl cation, Becke3LYP/6-31G\*.



**Fig. 4.** Bicyclo[2.1.1]hex-2-en-5-ylum Cations. Experiment: X-ray ((deloc-2,3,5)-endo-6-Chloro-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hex-2-en-5-ylum cation): reference (2e), values in parentheses. Ab Initio: Geometry ((deloc-2,3,5)-1,2,3,4,5,6-hexamethyl-bicyclo[2.1.1]hex-2-en-5-ylum cation): Becke3LYP/6-31G\*.

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