

Recent Studies of Carbocations

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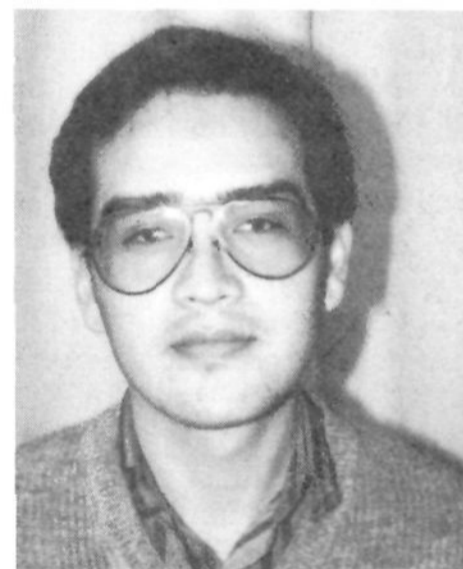
1. Introduction

Classical studies using stereochemistry, kinetics, and isotopic tracers in the exploration of reaction mechanisms of displacement reactions are featured in all organic chemistry textbooks, and carbocation intermediates are indicated in many cases. The main properties and reactions of carbocations were studied for some time in this way. For the past 20 years, however, it has been possible to learn more about carbocations through the preparation and study of many of them in solutions where they are indefinitely stable. Since the beginning of this period, NMR has been the most powerful and widely used experimental method to gain insight into the structures of, and rearrangement processes in these ions. Its use, supplemented by isotope effects and techniques for obtaining spectra in the solid state at low temperatures or, in a few cases, X-ray studies of crystalline salts, has greatly improved our detailed knowledge about their structures, relative energies, and rearrangement processes. Over this period, theoretical calculations have considerably increased in accuracy due to improvements in programs and computers. Comparison of experimental results with those of calculations has been instructive to both experimentalists and theoreticians. Since most calculations refer to the isolated cation in the gas phase, the close correspondence, in a number of cases, between experimental and theoretical results leads to the striking conclusion that solvent effects play a limited role on the relative energies of different equilibrium structures and transition states of carbocations.

The objective of this review is to cover some of the most relevant papers on carbocations published in the last five years,¹ in particular those related in some way to NMR studies.² The investigation of these ions remains active since new species with unusual structures or rearrangements continue to be reported. In addition, some long-investigated cations are still of concern be-



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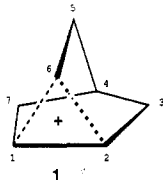


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cause of our increasingly more detailed questions involving the partial bonding in those ions loosely referred to as nonclassical and also because new or improved experimental techniques and theoretical methods are developed and applied to them.

The term "nonclassical ion" was originally coined to describe carbocations where a carbon is bonded to more than four neighboring atoms. Some of the bonds were then described as fractional instead of the typical single, double, and triple bonds of our textbooks. The one and a half bonds represented by resonance structures in allyl

cations had previously been accepted and were not included in this new description. The norbornyl cation is the prototype of this nonclassical category. The 1,2-shift or Wagner–Meerwein rearrangement required that a C–C bond migrate toward the cationic center of norbornyl. In this process, the original bond is broken and a new one is formed. The structure half-way along this pathway, 1, might have been considered to be an energy maximum and hence a transition state similar to those for many other bond-breaking or bond-making reaction steps. The 1,2-shift was known to be an ex-



tremely facile process for many carbocations and hence its barrier would have to be very low. However, Wilson³ and Winstein⁴ made the novel proposal that there was no barrier. In other words, the half-way structure was an energy minimum, an intermediate, and this was the most stable form of the ion.⁵ At the present time, a variety of experimental studies and theoretical investigations using high-level quantum mechanics, have strongly supported the conclusion that the stable structure for the norbornyl cation is nonclassically bridged.⁶ A number of other cases of 1,2-shifts of C–C, C–H, and other bonds have been studied where such nonclassical structures have been demonstrated to be the most stable form. However, there are many other cases of 1,2-shifts where the nonclassically bridged structure is a transition state. So much study and so much discussion of these cases is in the literature, that these bridged ions might now be called “classical” nonclassical ions.

1,2-Shifts are not the only types of carbocation rearrangements. Many hydride shifts may be described as 1,3, 1,4, 1,5, etc. Similar questions concerning bridging arise in these cases. In some of these systems, particularly where the shift occurs across a ring,⁷ or in a bicyclic system,⁸ structures have been clearly demonstrated to be bridged. There are also cationic systems where the rapid rearrangement processes do not easily fit into the category of a simple shift. In the $C_4H_7^+$ (cyclopropylcarbinyl or bicyclobutonium) ion, we know that there is a rapid rearrangement process among three degenerate structures which are each, in a sense, nonclassical. Other cases are known where it is likely that one nonclassical ion is rapidly rearranging to other nonclassical ions. The transition states for these processes are also nonclassical, but not of the simple type described above.

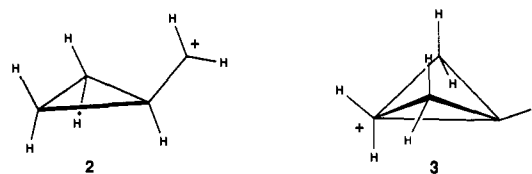
2. Theoretical Studies⁹

Calculations have been used in several ways in the study of carbocations. Ab initio and semiempirical methods can yield structural information, energies, and electron densities, and they can predict whether a structure is an energy minimum or a transition state. It has been found, however, that very high level ab initio calculations are needed in order to obtain results which are closely comparable with those of experimental studies, particularly in cases where it is probable that

the ions exist in the form of classical or nonclassical species. For these systems, the results of calculations usually change as the size of the orbital basis set is increased and/or electron correlation is included. This happens because their energy surfaces are very flat, and hence small changes in energy can alter the relative positions of the energy minima a great deal. A second use of ab initio methods involves calculation of vibrational frequencies that can then be used to calculate equilibrium isotope effects which, in turn, can be compared with the experimental data obtained from NMR studies on isotopically labeled ions. A third recent application of calculations in the carbocation area is the determination of theoretical NMR chemical shifts. Calculations have also been used, along with NMR, to study kinetic parameters for rapid carbocation rearrangements, by means of NMR line-shape analysis.

The recently developed IGLO (individual gauge for localized molecular orbitals) method allows the calculation of magnetic susceptibilities and chemical shifts of organic molecules.¹⁰ It has been successfully applied by Schindler to carbocations, although several restrictions apply. Due to the fact that the chemical shifts of carbocations are very sensitive to changes in geometry, it is advisable to carry out the computations with either the experimental geometry (if known), or with that obtained with very high level ab initio calculations. On the other hand, the agreement between calculated and experimental chemical shifts is very good for nonclassical carbocations. Nevertheless, the method does not take into account interactions with solvent or counterions and hence, for localized carbenium ions, the agreement is not as good. For them, the calculated chemical shifts are in general more deshielded than the experimental values. In a recent paper,¹¹ Schindler presents the calculated 1H and ^{13}C chemical shifts of several carbocations, ranging between CH_3^+ and 2-norbornyl. The chemical shifts calculated for the nonclassical structure of the 2-norbornyl cation (1) are in agreement with experimental NMR spectra.

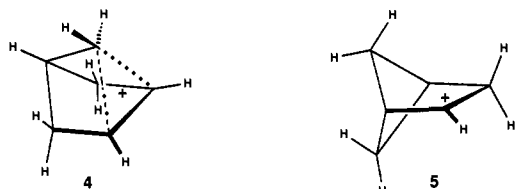
NMR isotopic perturbation studies,^{12,13} suggested that the $C_4H_7^+$ cation, obtained from cyclobutyl or cyclopropylcarbinyl precursors, exists primarily as three rapidly equilibrating cyclopropylcarbinyl ions (2) in equilibrium with three degenerate bicyclobutonium ions (3). These studies were interpreted as to indicate that



3 is the dominant species at equilibrium, although the participation of other species could not be ruled out. In any event, all structures and transition states of the ion must be within 2 kcal/mol or less of one another. Theoretical calculations have been used in trying to estimate points on the potential energy surface for this system, but the early attempts had limited success. Not until recently was the importance of using extended basis sets and the inclusion of electron correlation in the ab initio calculations shown to be extremely important to get reasonable results for this ion.¹⁴ HF/6-31G* calculations describe 2 and 3 as saddle points. However, at the MP2FULL/6-31G** level of theory,

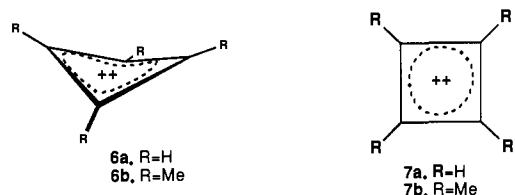
both structures appear as energy minima on the potential energy surface.¹⁵ At the MP4/6-31G**//MP2/6-31G* + ZPVE level, both ions have the same energy, with an interconversion barrier of 0.6 kcal/mol.¹⁵ A theoretical calculation of the ¹³C chemical shifts of both cations was carried out¹⁶ with use of the IGLO method,^{10,11} on the MP2/6-31G* optimized geometries. Comparison between experimental and calculated chemical shifts suggests again that the bicyclobutonium ion is predominant over the cyclopropylcarbanyl cation. From the chemical shift dependence on temperature and the calculated IGLO chemical shifts, **3** is predicted to be about 0.5 kcal more stable than **2**.¹⁶

The 2-bicyclo[2.1.1]hexyl cation is another system that has been considered to be rapidly equilibrating over a 3-fold energy surface via bridged or classical structures. An isotopic perturbation study^{17a} clearly favored the bridged structure **4**. An ingenious investigation of the solvolysis reaction using isotopic labeling ruled out the classical ion **5** as an intermediate.^{17b} Ab



initio calculations carried out at the MP3FC/6-31G*//MP2FULL/6-31G* + ZPVE level of theory¹⁸ agree with these results. Both structures are energy minima in the HF/6-31G* energy surface. NMR chemical shifts were calculated for them by using the IGLO method (DZ//MP2FULL/6-31G*), and the values thus obtained compared with experimental results. Again, the results are in much better agreement with the symmetrically bridged nonclassical structure **4** rather than **5**.

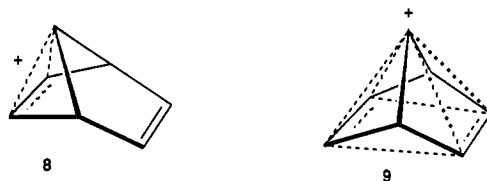
The IGLO method was used by Schleyer et al. to study the cyclobutadiene dication.¹⁹ Earlier ab initio²⁰ and X-ray crystallography studies of derivatives²¹ suggest that the puckered ring **6** is more stable than the planar structure **7**. Calculation of the chemical shifts



on the HF/6-31G* optimized structures, for the parent (**6a**,**7a**) and tetramethyl-substituted ions (**6b**,**7b**), was carried out with use of several basis sets. At the HF/6-31G* level of theory, **6a** is a transition state. Comparison between calculated and experimental chemical shifts for **6b** and **7b** suggests that the planar structure can be ruled out. The fact that the puckered structure is more stable was attributed to 1,2- and 1,3-stabilizing orbital interactions.

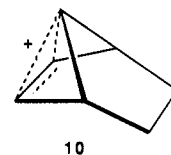
The IGLO method was also applied to the study of the 7-norbornadienyl cation.²² High-level ab initio calculations (MP2FC/6-31G*//6-31G*) confirm that the proposed structure with C_s symmetry **8** is more stable by 26.6 kcal/mol than that with C_{2v} symmetry

9, in agreement with earlier conclusions based on experimental results.²³ The calculated geometry shows



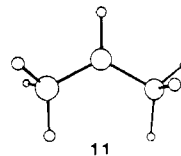
a large structural distortion of the skeleton when compared with the parent norbornadiene. The energy required to achieve this distortion is largely overcome by the stabilization gained through the bishomoaromatic interaction.

The chemical shifts calculated by IGLO (DZ//6-31G*)²⁴ for **8** are in close agreement with the experimental values, while those calculated for **9** (DZ//6-31G*) deviate substantially from the NMR data. Good agreement between theory and experiment is also found for the 7-norbornenyl cation **10**. Similar results were obtained with use of the GIAO method.^{10c,d}



Among the data that can be obtained from molecular orbital calculations, the vibrational frequencies can be used to predict equilibrium isotope effects. In the Born–Oppenheimer approximation, the potential energy surface is independent of isotopic substitution, but the vibrational levels depend on the mass of the atoms involved in the vibrational mode. Recently, a computer program (QUIVER) was developed, which calculates equilibrium isotope effects²⁵ by using the cartesian force constants obtained with the GAUSSIAN series of program packages.²⁶ By using this methodology, the effect of isotopic substitution on rearrangement processes of carbocations can be determined and compared against experimental results. The method was applied to the cyclopropylcarbanyl–bicyclobutonium and bicyclo[2.1.1]hexyl cation systems.²⁵ The calculated isotope effects are in excellent agreement with the experimental values,^{12,27} and support **3** and **4** as the major contributors to the structure of these ions.

High-level ab initio calculations (MP4FC/6-311G**//MP2FULL/6-311G** + ZPE) find a single energy minimum for the 2-propyl cation **11**.²⁸ The structure has C_2 symmetry, with the methyls slightly twisted in the same direction. The calculated ¹³C

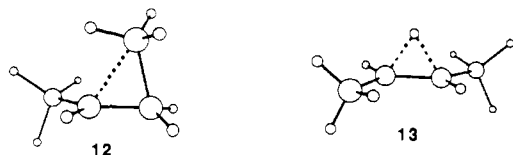


chemical shifts (IGLO) agree with experiment only for this geometry. The conformational preference of the methyl groups is attributed to enhanced hyperconjugation with one hydrogen on each methyl; the dihedral angle between this hydrogen and the empty p orbital is 1.4°, while the corresponding C–C–H angle is 92.7°. More recent calculations at the MP2-R12 (second-order Møller–Plesset perturbation theory with r_{12} -dependent

terms) level confirm these results.²⁹

Previous NMR studies of the 2-butyl cation revealed that it undergoes very fast hydrogen scrambling.³⁰ Because this rearrangement could not be slowed down enough to see separate signals in ¹³C NMR even in the solid state at -190 °C, the energy barrier for this process has been estimated to be less than 2.4 kcal/mol.³¹ Splitting of the ¹³C NMR peaks of the central carbons, when a methyl was substituted by deuterium, was observed, but only about one quarter the value expected for the classical ion. This was interpreted as suggesting that two structures in rapid equilibrium are present, one of them a hydrogen-bridged structure 0.4 kcal/mol more stable than the other species.³² This ion was also studied by Johnson and Clark using ESCA.³³ They interpreted the results as indicating a methyl-bridged structure for the ion; however, a major problem for this and other ESCA studies of ions is that there is no independent way of demonstrating the identity and purity of the material in the top 30–50 Å of sample, which is all that ESCA looks at.

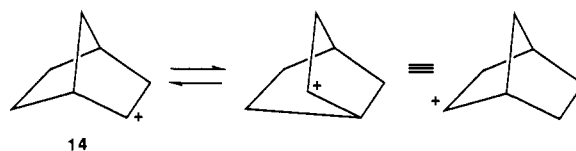
A series of ab initio calculations were made for this system by using different basis sets and different levels of electron correlation.³⁴ Two energy minima were found. One of them corresponds to one form of the classical cation (12 that is distorted to favor C–C hyperconjugation, and which could be regarded as partially methyl bridged. The second structure found was the symmetrical H-bridged cation 13. At the highest level of theory used (MP4SDTQ/6-311G**//MP2FULL/6-31G**), 12 is more stable than 13 by 0.78 kcal. Introduction of zero-point energies, however, makes 13 more stable by 0.31 kcal/mol, in agreement with experimental results.³² The possibility that differential solvation could invert the relative stabilities of 12 and 13 was also considered. Use of the self-consistent reaction field (SCRf) method³⁵ suggests that 13 should be preferentially solvated, a fact that might make this species even more stable in solution.



Calculation of the chemical shifts using the IGLO method gave very good agreement with experiment only for the geometry calculated for 13. The authors concluded that the 2-butyl cation is H-bridged, and that the ESCA results could be explained by surface effects, that is, the species observed in this experiment is not the same as that observed in solution.

Dewar and Merz,³⁶ following a proposal previously made by Fong,³⁷ suggested that the NMR spectrum of 2-norbornyl cation, which is that expected for the symmetrical nonclassical ion 1 even at 5 K,³⁸ could be explained by heavy atom tunneling. The assumption was that, because of tunneling, the rate of interconversion between the two classical 2-norbornyl cation structures 14 (Scheme I) is so fast that an averaged (fast-limit) NMR is obtained. However, Saunders and Johnson³⁹ pointed out that tunneling is a coherent rather than a random process, which therefore should not broaden NMR lines, but instead can lead to additional splitting and shifts of spectral lines, eventually yielding a single

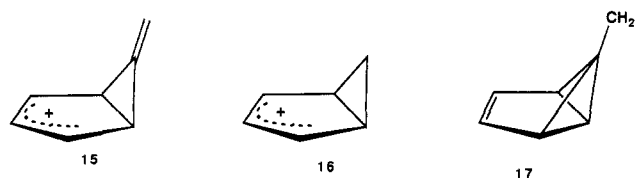
SCHEME I



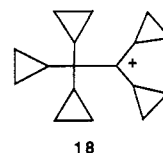
sharp line if the “tunneling frequency” is high enough. The absence of additional bands could also be explained by very high frequency tunneling at all temperatures, but this does not seem likely to occur. In other cases, where definite tunneling phenomena (light-atom) have been observed by using NMR, the tunneling frequencies, and hence the observed splittings, are sensitive functions of temperature and isotopic substitution. The spectrum of norbornyl cation is unchanged with temperature and isotopic substitution. Therefore, the spectra of the 2-norbornyl cation were considered more consistent with the nonclassical structure 1 than with 14.

3. Novel or Unusual Structures for Cations

The 6-methylenebicyclo[3.1.0]hex-3-en-2-yl cation (15) was generated from the corresponding chloride.⁴⁰ This ion might have been expected to rearrange to the isomeric benzyl cation because bond additivities predict a heat of reaction of approximately 63 kcal/mol. However, it was found to be stable up to -70 °C. The NMR results suggest that the methylenecyclopropane fragment migrates around the five-membered ring. From the changes suffered by the NMR spectrum in the range -110 to -70 °C, a line-shape analysis was performed by using the KUBO⁴¹ program. These calculations gave as a result an activation energy of 10.6 ± 0.2 kcal/mol for the circumambulation. This process is 2.2×10^7 times faster than that observed for the bicyclo[3.1.0]hex-3-en-2-yl cation (16).⁴² The difference was explained by proposing that the exocyclic olefin directly participates in the sigmatropic rearrangement, through a hypothetical dicyclopropylcarbanyl species 17. Because no conversion to the benzyl cation was observed up to the decomposition temperature (-70 °C), the energy barrier for the process was estimated to be at least 11.5 kcal/mol. Such a high barrier was attributed to the orbital-symmetry-forbidden character of the rearrangement.



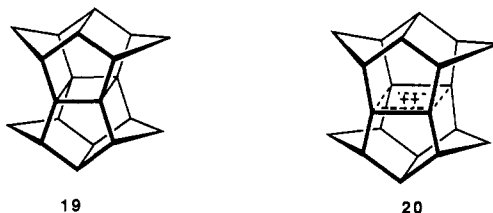
Timberlake et al.⁴³ prepared the pentacyclopentyl-ethyl carbocation (18). Its ¹³C NMR spectra show all five cyclopropyl rings to be equivalent down to -100 °C.



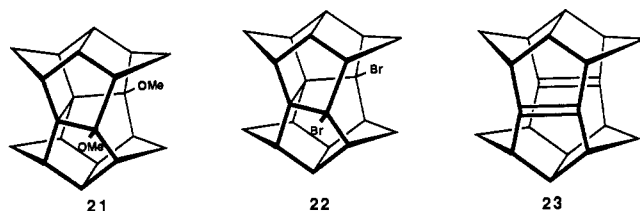
To address the question of whether the cation is classical or nonclassical, they used the Schleyer–Lenoir–Olah approach,⁴⁴ which consists in comparing the sum

of all ^{13}C resonances in the ion to that of the corresponding hydrocarbon. From the result, the carbocation was described as a classical ion in rapid interchange.

One of the suggested synthetic routes to dodecahedrane involved acid-catalyzed rearrangement of [1.1.1.1]pagodane (19). However, treatment of 19 with $\text{SbF}_5/\text{SO}_2\text{ClF}$ at -78°C , gave as result slow oxidation (through a proposed initial formation of radical cations) of pagodane to a unique dication 20, with the D_{2h} symmetry of the parent system.^{45,46} Both, ^1H and ^{13}C NMR



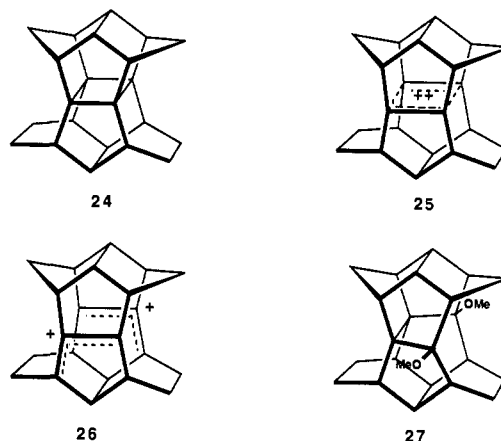
spectra consist only of four signals. The ion was found to be stable even at room temperature for several hours, and the NMR spectra were not temperature-dependent down to -130°C . From the deshielding of the ^{13}C NMR signals, both positive charges were located mainly at the carbon atoms of the central cyclobutane ring. On quenching the ion with MeOH , only one dimethoxylated derivative 21 was formed, from which the X-ray structure could be obtained. The dication was also formed from two other precursors, by (a) ionization of the dibromide 22 and (b) oxidation of the corresponding diene 23. On the basis of the experimental results, several proposed structures for the dication were discarded.



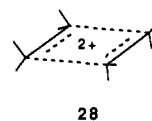
The behavior of [2.2.1.1]pagodane (24) was also investigated. In this case, the strain imposed in the middle section of the structure is smaller than in 19. Treatment of 24 with SbF_5 gave as a result a species 25, very similar to that found for the smaller pagodane. However, even at -78°C more than one set of signals were found. On heating at 0°C , the ion decomposed. At -20°C a new species was formed, which was tentatively assigned to a bisallylic dication with C_2 symmetry 26. On quenching with methanol, a dimethoxylated product 27 was presumably formed; however, the reaction was not clean.

Several other polycyclic compounds incorporating a fixed, planar cyclobutane unit were also investigated. None of them gave results analogous to those found for the pagodane systems. This fact, along with the lesser stability of 25, indicates the important influence of the geometry of the four-membered ring on the nature of the cationic system.

On the basis of the experimental results, the pagodane dications are described as "...the first representatives of a novel class of 2π -'aromatic' pericyclic systems, topologically equivalent to the transition state for the Woodward-Hoffmann 'allowed' cycloaddition...of



ethylene to ethylene dication...⁴⁶ Ab initio STO-3G on the parent $\text{C}_4\text{H}_8^{2+}$ 28 and semiempirical (MNDO) calculations on the pagodane systems further support this point of view.

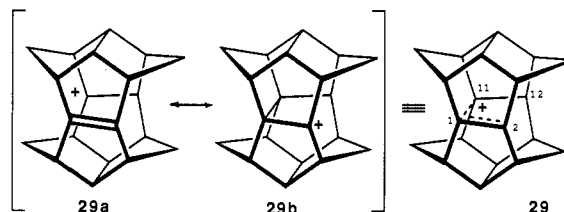


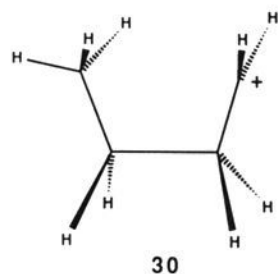
For 19, the geometry of the four-membered ring is such, that it resembles the planar transition state of the cycloaddition. On the other hand, 24 has a more relaxed structure, giving as a result loss of aromatic character. As criteria for aromaticity, the authors offer evidence of a ring current on the basis of the chemical shifts of the dication, along with its already discussed stability.

The 2-secopagodyl monocation (29) was generated from three different precursors.⁴⁷ The ^1H and ^{13}C NMR spectra show in all cases a single species with C_s symmetry. From the 12 ^{13}C resonances, the more interesting are those corresponding to the carbons situated in the plane of symmetry of the molecule. The chemical shifts for C_2 , C_1 , and C_{11} are 279.2, 129.1, and 140.6 ppm, respectively; in contrast, all carbons of the parent secopagodane are found below 70 ppm. These chemical shifts strongly suggest C-C hyperconjugation of the C_1 - C_{11} σ -bond with the cationic center at C_2 , with a large delocalization of the positive charge toward C_{11} (Scheme II). semiempirical calculations (MNDO) further support this idea. The optimized geometries show a shortened C_1 - C_2 bond, a lengthened C_1 - C_{11} bond, and a small C_2 - C_1 - C_{11} angle relative to the hypothetical 1-butyl cation (30) optimized at fixed cis geometry. The special characteristics of 29 are attributed to (a) strain imposed by the carbon skeleton and (b) perfect coplanar arrangement of the C-C bond with the empty p orbital.

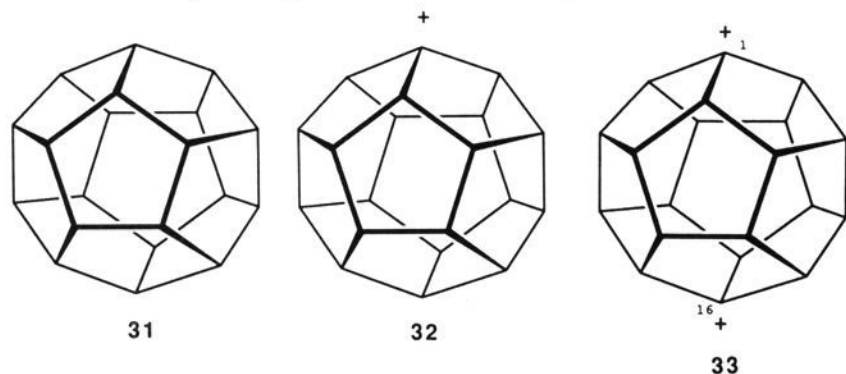
In order to test the possible functionalization of dodecahedrane (31) through the transient generation of dodecahedryl cation (32), Olah and co-workers gener-

SCHEME II



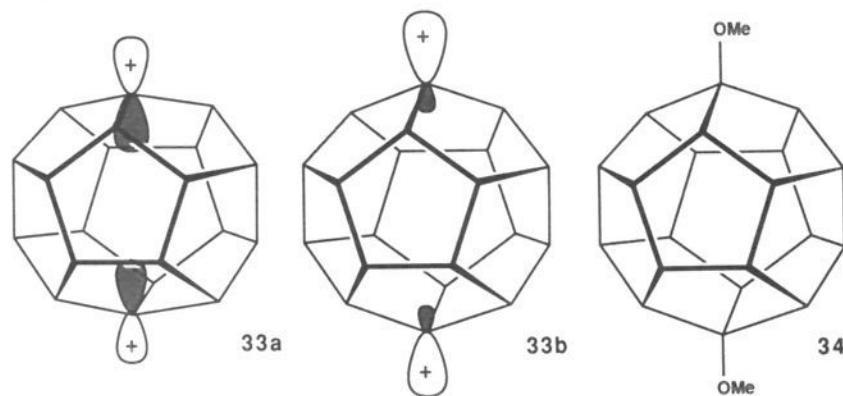


ated it under long-lived conditions. Surprisingly, the cation is very easily oxidized to the 1,16-dication **33**.^{48,49}



32 was prepared in $\text{SbF}_5/\text{SO}_2\text{ClF}$ at -78°C from the corresponding Cl or OH precursors. The ^1H NMR spectrum presents only three sets of signals in the ratio 3:7:9. In ^{13}C NMR, the cation shows six lines, with the cationic carbon having a chemical shift of 363.9 ppm. From this data, the C_{3v} symmetry was assigned to the ion. Because no changes in the spectra were seen in warming up the solution to 0°C , the kinetic barrier of the 1,2-hydride shifts was estimated to be at least 15 kcal/mol.

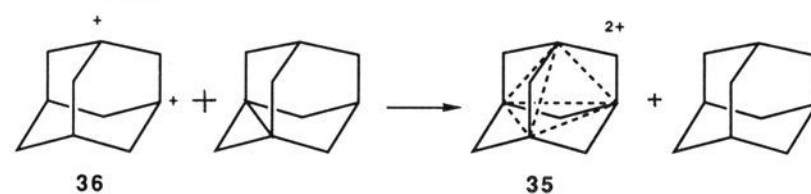
After the ion stood for several hours at -50°C , the ^1H NMR spectrum changed from three to only two sets of signals, while the ^{13}C spectrum was reduced to three lines. The ^{13}C chemical shifts of the cationic carbons was 379.2 ppm. From the spectra, the new species was identified as the dodecahedryl dication (**33**) with D_{3d} symmetry. It was presumably formed by oxidation of the C–H bond at position 16. The dication was also formed as the only species, from an isomeric mixture of dodecahedryl dibromides. Quenching the dication with methanol gave, as the only product, 1,16-dimethoxydodecahedrane (**34**).



The far downfield chemical shifts of the cationic carbons in both ions, which are the largest chemical shifts ever reported for a carbocation, suggested extremely localized positive charges. However, the chemical shift additivity criterium⁴⁴ suggests a cage-shielding effect whose origin could not be determined. The chemical shifts of the cationic centers can be attributed to (a) the inability of the dodecahedryl system to accommodate a planar sp^2 carbon and (b) the lack of significant C–H as well as C–C hyperconjugative stabilization.

MNDO semiempirical MO calculations were carried out for both systems. For **32**, the structure shows a

SCHEME III



highly deformed structure, with an almost planar cationic center. The hydrogens at the adjacent positions, which might be expected to stabilize the cation by hyperconjugation, are bent away of it, being the calculated $\text{C}^+-\text{C}-\text{H}$ angle 115° . For **33**, MNDO predicts the cationic carbons to be almost sp^3 hybridized. This was interpreted as a result of Coulombic repulsion between the positively charged centers. For a hypothetical structure with cationic sp^2 carbons **33a**, the through-space interaction is expected to be quite large, causing the cationic centers to bend away from each other, as shown in **33b**.

The huge energy barrier to 1,2-hydride shifts is striking. Similar shifts in acyclic tertiary ions have barriers around 3.5 kcal/mol. Here, the adjacent C–H bonds are perfectly aligned, but the p orbitals of the two carbons involved in the migration can not be parallel, as they must be in an ideal transition state. In other words a geometry similar to that of an olefin is required.

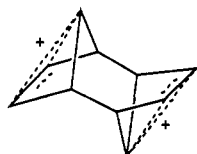
MINDO/3 calculations predicted the nonclassical 1,3-dehydro-5,7-adamantenediyl dication (**35**) to be 47.0 kcal/mol more stable relative to the classical analogous **36** and 1,3-dehydroadamantane (Scheme III).⁵⁰

35 was generated by dissolution of 1,3-dehydro-5,7-difluoroadamantane in $\text{SbF}_5/\text{SO}_2\text{ClF}$ below -80°C . The resulting ion was stable up to 0°C . The NMR data shows remarkable upfield shifts despite the positive charges. The ^{13}C NMR shifts are 6.6 and 35.6 ppm for the bridgehead and methylene carbons, while the ^1H NMR shift is 3.8 ppm for the methylene hydrogens. These values by themselves give very strong indication of the nonclassical nature of **35**. In addition, the methylene coupling constant, $J_{\text{C}-\text{H}} = 165$ Hz, confirms the deformation of the C– CH_2 –C angle pointed out by theoretical calculations (87.3° at the 3-21G level).

For classical cations in rapid equilibrium, the average chemical shift of the bridgehead carbons is predicted to be 169 ppm, more than 160 ppm away from the observed value. In addition, the difference between the sum of the ^{13}C chemical shifts in the dication and the correspondent hydrocarbon is expected to be around +800 ppm for the classical species. The experimental difference is -214 ppm. IGLO ^{13}C chemical shifts (DZ//3-21G) calculated for the nonclassical structure are in remarkable agreement with the experimental values as well.

Theoretical calculations (3-21G//3-21G) show that the overlap between the bridgehead carbons is 0.38, further evidencing delocalization of the two electrons between four carbons in a nearly spherical topology. For the authors, this is another example of three-dimensional aromaticity, in which Hückel's $4n + 2$ rule applies to "interstitial" instead of π electrons.

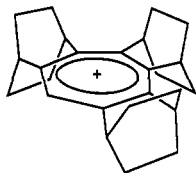
Olah and co-workers prepared the *anti*-tricyclo-[4.2.1.1^{2,5}]deca-3,7-diene-9,10-diyl dication (**37**) by dissolution of the corresponding 9-*endo*-10-*endo*-diol in $\text{SbF}_5/\text{SO}_2\text{ClF}$ at -78°C .⁵¹ The ^1H and ^{13}C NMR spectra showed only three absorptions, with chemical shifts shielded from those of the parent diol. In ad-



37

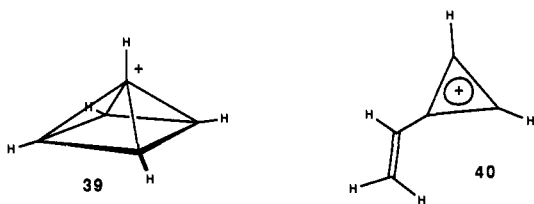
dition, the J_{C-H} 's are all between 169 and 220 Hz. These results were interpreted as to indicate the formation of a highly symmetrical structure in which two bis-homoaromatic cations are "sandwiched" together. Comparison of the chemical shifts with those of the 7-norbornenyl cation (10), show that in 37 they are more deshielded, probably as a result of the presence of two adjacent positive charges. The chemical shifts were found to be independent of temperature between -120 and -40 °C, ruling out equilibrium processes. The authors conclude that 37 is the first example of a long-cyclic four-ribbon four- π -electron [0,2,0,2] aromatic system.⁵²

One of the most stable carbocations ever reported, the 1,2:3,4:5,6-tris(bicyclo[2.2.2]octeno)troplium ion (38), was recently described.⁵³ The half-neutralization point of the ion is reached at pH 13.0, meaning that it does not react with bases such as PhS^- or PhO^- . Its stability is attributed to inductive effects and enhanced hyperconjugation of the aromatic system with the C-C σ -bonds which are in position almost parallel to the atomic p orbitals of the ring.



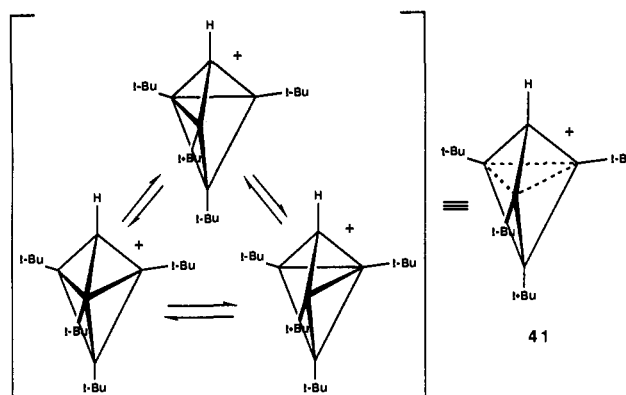
38

Earlier theoretical calculations found an energy minimum for a pyramidal arrangement (39) of the carbon atoms in the $(\text{CH})_5^+$ ion.⁵⁴ However, more recent high-level calculations indicate that it should prefer a planar vinylcyclopropenium geometry 40.⁵⁵ Maier



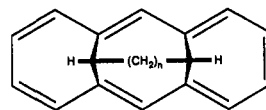
and co-workers⁵⁶ prepared the tetra-*tert*-butyl-substituted precursor and generated the ion in superacidic conditions in order to carry out NMR experiments. The NMR spectra obtained below -100 °C is consistent with an unsymmetrical pyramidal arrangement. Above this temperature, the signals for carbons 1-3 broaden and eventually disappear. At temperatures higher than -80 °C, the NMR spectra are consistent with a highly symmetric species 41. The authors propose an equilibrating system in which three nonclassical equivalent structures interconvert rapidly above -80 °C (Scheme IV). However, no averaged signal for C_{1-3} was observed in the temperature range of the experiment. The peaks of the *tert*-butyl groups also seem to be in agreement with this interpretation. The fact that the ion prefers a "spherical structure" rather than being planar, as in

SCHEME IV

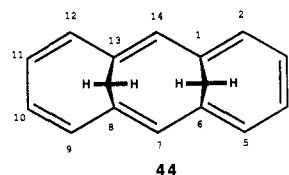


the unsubstituted ion, is attributed to the steric repulsion between the *tert*-butyl groups.

Recently, Michl et al. studied the behavior of several 1,6:8,13-bridged [14]annulenes in $\text{SbF}_5/\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ using ^1H and ^{13}C NMR.⁵⁷ For the 1,6:8,13-propanediylidene 42, 1,6:8,13-butanediylidene 43, and *syn*-1,6:8,13-bismethano 44 derivatives, the NMR data showed easy protonation of the rings at position 7. On



42, n=1
43, n=2
45, n=0

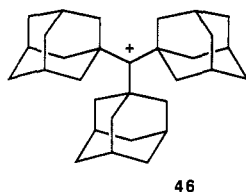


long standing or on warming, the cations were oxidized to the corresponding dication by loss of hydride. On the other hand, the 1,6:8,13-ethanediylidene 45 showed a different behavior. The NMR spectra supported protonation either at positions 2 or 3. The monocation could not be generated at high concentrations, as it was the case for the other systems. Additionally, there was no further oxidation to the dication. The protonated species decomposed on standing or warming.

The differences in behavior between the annulenes were rationalized in terms of the geometry of the systems. Because 45 is the most planar of the annulenes studied, it should have the least transannular interaction, a fact that makes it the most "annulene-like" system. On the other hand, all the other molecules have strong transannular interaction and hence are more "anthracene-like". This factor, along with the strain of the rings, makes the difference in the site of protonation. Additionally, because the dication is a 12-electron system and hence antiaromatic, the molecule behaving the most like an annulene should be the more unsuited to become a stable entity.

Recently Olah et al. reported the preparation of one of the most sterically hindered trialkyl cations observed to date, the tris(1-adamantyl)methylcation (46).⁵⁸ It was generated by treating the parent chloride with $\text{FSO}_3\text{H}/\text{SbF}_5$ in SO_2ClF at -78 °C. In contrast with the tris(*tert*-butyl)methyl cation which is very unstable and

cannot be observed under long-lived conditions,⁵⁹ 46 is stable enough to obtain its NMR spectra. The ¹³C chemical shift of the cationic carbon is 327.1 ppm, in the normal range of tertiary classical carbocations. The stability of 46, despite the high strain involved in having the three big adamantyl groups so close to one another, is attributed to the structural constraints of the adamantyl cages.

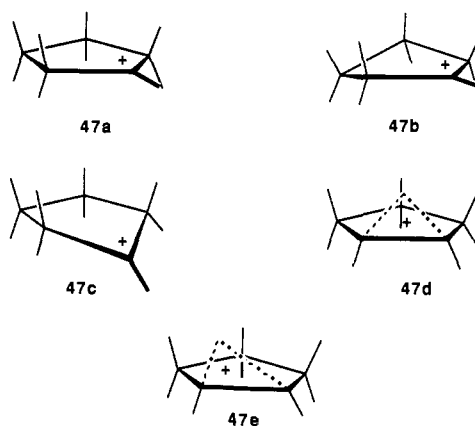


4. Unusual Rearrangement Reactions

In a very interesting communication, Mayr and Koschinsky describe the ¹H and ¹³C NMR data of the nonamethylcyclopentyl cation (47).⁶⁰ Generated from nonamethylcyclopentanol in FSO₃H/SbF₅SO₂ClF at -90 °C, the cation showed a single peak in the ¹H NMR spectrum, indicating total scrambling of the methyl groups. Cooling the ion to -137 °C resulted in splitting of the methyl peak into two resonances with relative intensities 5:4. From line-shape analysis, a barrier of 7 kcal/mol (at -120 °C) was estimated for the process that interchanges the two types of methyl groups. ¹³C NMR showed similar results for the methyl carbons. However, the ring carbons remain as a sharp singlet even at -135 °C, indicating a barrier of less than 2.5 kcal/mol for the circumambulatory process (assuming that the carbons cannot really be the same through static symmetry). In Mayr's words: "These spectra indicate that rapid circumambulatory methyl migrations take place, while a set of four methyl groups remains separate from a second set of five methyls..."

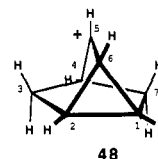
On the basis of the NMR results, the planar classical cation 47a was ruled out since a fast rearrangement involving methyl shifts would then lead to a complete scrambling of all nine methyls. Several other structures for the ion were considered to possibly account for the unexpected observations: (a) An ion with a nonplanar five-membered ring and with C₂ symmetry 47b. This structure was discarded on the grounds of molecular mechanics calculations. (b) A cation with a nonplanar five-membered ring and C_s symmetry 47c. (c) A methyl-bridged cation 47d in which the 1,2-methyl migrations occur with inversion at the ring carbons (migrations occurring with retention could give the same result). (d) A partially bridged structure 47e (somewhere in between 47a and 47d, behaving similarly to 47d).

Although no conclusive proof of the structure of the ion was obtained, the authors proposed 47e to be the most probable, on the basis of the observed ¹³C chemical shifts. Nevertheless, they could not exclude 47c or 47d. It seems unlikely to us that ions of the character of 47d or 47c would scramble the methyl groups much faster than if they went through the equivalent of the planar classical structure. It seems much more likely that a nonclassical ion 47d could scramble methyls (with inversion or retention) without going through the planar classical geometry. Since it is necessary to go through the geometry of 47d in the methyl scrambling process,



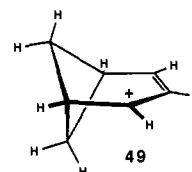
it seems more complicated than required to propose that 47e is a minimum on the energy surface. Having a series of bridged, nonclassical ions interconverting (probably) with inversion is similar to the series of rearrangements known to occur in the initially formed cation in the conversion of squalene epoxide to triterpenes.⁶¹ It seems likely in that case as in this, that the species interconverting are bridged ions rather than open carbocations.

It has been known for some time that 3-nortricyclyl and 2-norbornenyl halides give the same cation when treated with SbF₅.^{62,63} The NMR spectrum of the ion shows it to be either a symmetric species or equivalent structures in rapid equilibrium. Data derived from chemical shift additivity and isotopic perturbation studies support the idea that its structure is best represented by a single tricyclic species with C_s symmetry, the nortricyclyl cation 48. It is also known that at least three degenerate rearrangement processes occur in the ion, which scramble both, the ring carbons and the ring hydrogens.

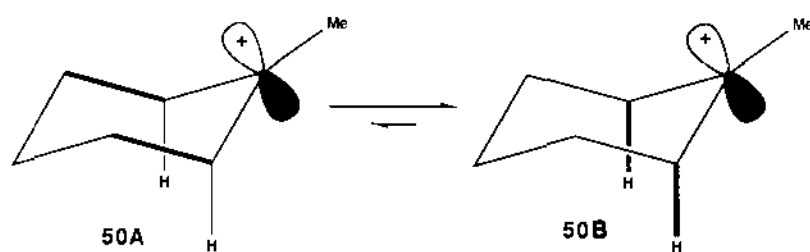


Several deuterium- and ¹³C-labeled nortricyclyl and norbornenyl halides were synthesized and dissolved in SbF₅/SO₂ClF.⁶⁴ The scrambling processes were followed by integration of the ²H and ¹³C NMR spectra as a function of time. From the changes observed in the spectra, scrambling paths were proposed for the two faster rearrangements, and the rates for each process were calculated, from the obtained data, by using the Runge-Kutta numerical method.

The first rearrangement studied is that which scrambles the carbons in the ring. It was found to occur, at a rate slow enough to be readily monitored by NMR, at temperatures between -70 and -60 °C. The activation energy was estimated to be 16.9 ± 1 kcal/mol if the value log A = 14 is assumed. From the scrambling pattern, it is proposed that the skeletal reorganization occurs via the bicyclo[3.1.1]heptenyl cation (49). Ab



SCHEME V

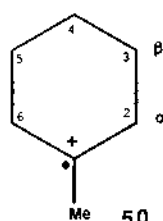


initio calculations (MP3/6-31G**/6-31G*) find **49** to be an energy minimum (frequency analysis at the 6-31G* level) 5.3 ± 1 kcal/mol above **48**. The activation energy needed to go from **48** to **49** is thus estimated to be around 11.6 kcal/mol. Attempts to generate **49** from the corresponding bromide were unsuccessful; only **48** is observed. The experimental barrier for this rearrangement is then calculated to be less than 12 kcal/mol, in agreement with the calculated value.

The second scrambling process occurs at a rate slower than that of the skeletal rearrangement and was monitored between -60 and -40 °C. It involves the 3,7-exo hydrogens. The scrambling pattern is in accord with a 3,2-hydride shift. By using the methodology mentioned previously, the activation energy was estimated to be 18.4 ± 1 kcal/mol. The third rearrangement scrambles the 3,7-endo hydrogens. This process is much more slower and is not detected below 0 °C.

5. Distortion of Carbocations—Minor Forms in Equilibrium

Several years ago,⁶⁵ it was reported that the 1-methylcyclohexyl cation (**50**) appeared to exist as a mixture of chair and twist-boat conformers. This

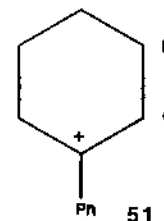


followed from the observation of the temperature dependence of ^{13}C chemical shifts of the carbons β (C_3) to the cationic center, along with extrapolation to the limiting chemical shifts and their comparison with those of model chair and twist-boat carbocations. We will call the structure with the low-field β -carbons **50A**, and that with the high-field β -carbons **50B**. A more careful analysis was recently done on the ion,⁶⁶ as a result of Lambert's observation⁶⁷ of temperature dependence of ^{13}C NMR shifts in molecules in which it is not possible to have any equilibrium process going on.

Several substituted 1-methylcyclohexyl cations were studied. Complete deuterium substitution at C_2 and C_6 of the parent, and some methyl-substituted ions showed an isotopic perturbation for those substituted at C_3 and/or C_5 , with the β -carbon shifted downfield. On the other hand, those cations substituted at C_4 had no significant isotope effect. A comparison between chemical shifts of the β -carbons, after correction for substitution, showed a wide range of values. This is in contrast to the approximately constant chemical shift expected for a single structure where no equilibrium is involved. It was also observed that the 4-substituted cations had a high-field shift for the β -carbon (hence

being very similar to **50B**) with no temperature dependence; while those cations substituted at C_3 and/or C_5 had a low-field shift of the β -carbons (tending to be similar to structure **50A**), which was temperature dependent.

A similar series of experiments carried out on 1-phenylcyclohexyl (**51**) cations showed them to be basically representable by a single structure. All these



results undoubtedly indicate that the 1-methylcyclohexyl cation is involved in an equilibrium process; however, the barrier was estimated to be less than 5 kcal/mol, since NMR line broadening was never observed.

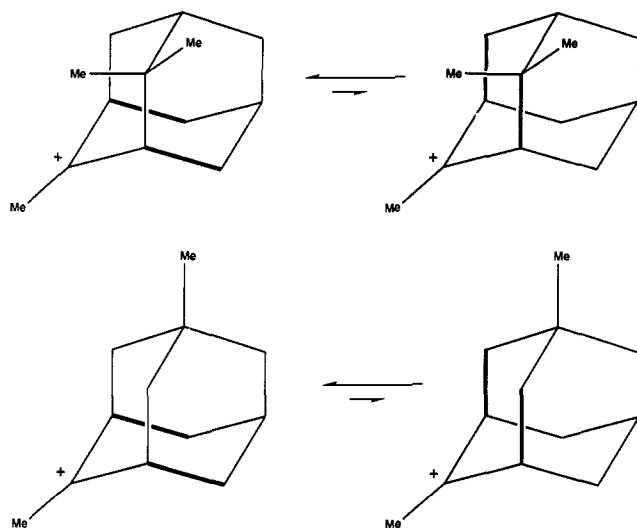
From the temperature-dependent chemical shifts, thermodynamic data were derived for the cyclohexyl cations. Van't Hoff plots allowed the estimation of the chemical shifts of the β -carbons in **50A** and **50B**, along with ΔH and ΔS values for the equilibrium. The ΔS was found to be very similar for all the ions, the equilibrium being predominantly determined by ΔH . It was also found that substitution at C_3 favors **50A**, while substitution at C_4 disfavors it.

After a careful analysis of all available data, it is finally concluded that both **50A** and **50B** isomers have a basic chair cyclohexane structure and not chair and twist-boat as previously suggested. It is proposed that in order for them to be different, **50B** has sizeable $\text{C}\alpha\text{-H}$ hyperconjugation, while data on **50A** is consistent with extensive $\text{C}\alpha\text{-C}\beta$ hyperconjugation (Scheme V). It is also proposed that these two effects operate as "... an either/or phenomenon rather than a mutually operational interaction...". Evidence was also found that the counterion might have to be included in the final description of the ion.

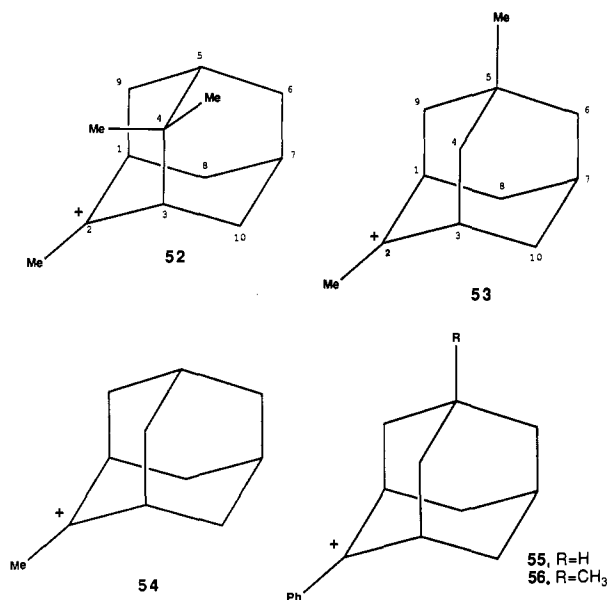
Looking for a better understanding of the phenomenon, Sorensen et al.⁶⁸ studied 2-methyl-2-adamantyl cations. If the same event were to occur, there would be a choice between two $\text{C}\alpha\text{-C}\beta$ hyperconjugation effects. This could be observed only if the symmetry of the ion is broken. The systems chosen were 2,4,4-trimethyl- and 2,5-dimethyl-2-adamantyl (**52** and **53**, respectively) cations. The ions were prepared from alcohol or chloride precursors in several acid solvents. The ^{13}C NMR was practically the same in all cases, showing no evidence of tight ion pairs.

For **53**, the ^{13}C NMR shifts of both β ($\text{C}_8, \text{C}_{10}$) and β' (C_4, C_9) carbons show a large temperature dependence, but in opposite directions. They have a separation of 17 ppm at 133 K and only of 7 ppm at 293 K. The high-field peak was assigned to $\text{C}_4\text{-C}_9$, and the low-field peak to $\text{C}_8\text{-C}_{10}$. There is also a moderate temperature dependence for C_2 and a much smaller dependence for other carbons. In **52**, the β carbons show once more the largest temperature dependence. $\text{C}_4\text{-C}_9$ have again positive shifts, while they are negative for $\text{C}_8\text{-C}_{10}$. C_2 is temperature dependent as well. Additionally, for the parent 2-methyl-2-adamantyl cation **54**, the only temperature-dependent chemical shift is that of C_2 . On the other hand, the NMR spectra of 2-phenyl- and 2-phenyl-5-methyl-2-adamantyl cations **55** and **56** show

SCHEME VI



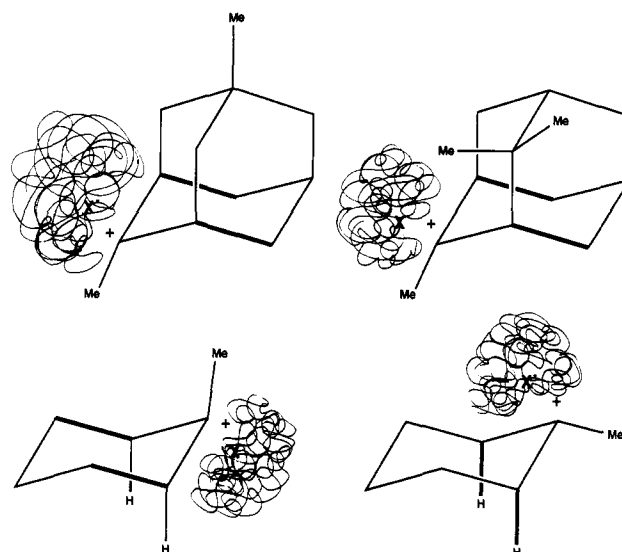
that they are fairly "normal", without the much larger effects observed in 52 and 53.



When comparing the chemical shifts of the methyl-substituted cations against those of the parent ion, it is possible to observe that all but the β -carbons have very similar values. In the authors' words, "... one has a significant chemical dichotomy between β -carbons situated on opposite faces of the 2-adamantyl frame...two carbons are shielded and two are deshielded." One might propose that substitution on one face of the ring system has perturbed the C-C hyperconjugation, in such a way that only one face is preferentially involved. However, the temperature dependence of the chemical shifts suggests the presence of two different structures in very rapid equilibrium. This equilibrium would consist in hyperconjugation of C^+ with the β or β' carbons, with the side of the molecule (C_8-C_{10}) not bearing substituents being preferred (Scheme VI). It is also suggested that the parent ion should undergo the same kind of equilibrium, in this case being $K = 1$.

MNDO calculations on the substituted ions found a single energy minimum, essentially planar at C^+ . This was taken as an evidence that in the gas phase, the equilibrating structures do not exist, and hence, in solution, the solvent and/or counterion should play an

SCHEME VII

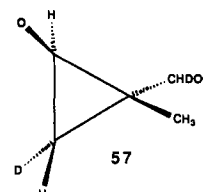


important role in the structure of the ion. It is concluded that the studied carbocations are able to delocalize the positive charge at C_2 by having preferential solvation on one face, that bearing the substituents. This should cause a slight pyramidalization of the cationic center, resulting in a rise in energy that would be overcome by a better alignment of C^+ with the C-C bonds involved in the hyperconjugation. MNDO studies on the 1-methyl-cyclohexyl cation show that small pyramidalizations of C_2 do not cause a large change in energy. It is also suggested that the results observed for the methylcyclohexyl cations,⁶⁶ can be explained by a similar argument (Scheme VII).

It can be concluded that the "normal" NMR data of the phenyl derivatives can be explained by using the pyramidalization argument as well. Hyperconjugation is a means of stabilizing a cationic center. In the case of the phenyl ions, the cationic center is already highly stabilized by the phenyl ring and the hyperconjugation effect, and hence pyramidalization, is not important.

Even though NMR and isotopic perturbation data has been interpreted as favoring a nonplanar bicyclobutonium structure ($C_5H_9^+$),⁶⁹ as the major contributor to the equilibrium of the methylcyclobutyl cation, the planar structure could not be ruled out. For a bicyclobutonium ion the equivalence of the methylene hydrogens can be explained, along with the interchange of the methylenes, by either a planar structure or a puckered ring that is inverting rapidly and hence interconverting the endo and exo hydrogens. Isotopic perturbation with only one deuterium affects both processes, and the observed isotope effect^{69c} could not be considered as conclusive evidence of the nonplanarity of the ion.

To avoid interference of the methylene interchange, the trilebeled $C_5H_6D_3^+$ cation was prepared from the alcohol precursor 57 in SbF_5/SO_2ClF .⁷⁰ If the structure



is planar, no isotope perturbation should be observed. On the other hand, for a nonplanar structure the presence of two deuteriums on one side of the ring should produce an isotope effect. ^1H NMR of the ion shows two peaks in a 2:1 ratio for the methylene protons, shifted downfield from the corresponding methylene peak in the unlabeled material, and with a small temperature dependence. This splitting unambiguously demonstrates that the methylcyclobutyl cation is nonplanar. Nevertheless, it was not possible to estimate the contribution of the methylene interchange to the isotope effect. On the other hand, the downfield shift of the methylene peaks seems to indicate the presence of a minor species in equilibrium with the major isomer, the equilibrium being perturbed by the deuterium.

6. Intrinsic Isotope Shifts in the NMR

It is well known that substitution of hydrogen by deuterium causes shifts in the ^{13}C NMR peaks of both neutral and cationic structures. In an attempt to understand the nature of these isotope effects, Servis and Domenick⁷¹ carried out ab initio calculations at the STO-3G level of theory on several molecules. They tried to model the isotope effects by examining the impact of the artificial modification of the C-H bond length on the electron density at each nucleus in the molecule, with the assumption that shortening of the bond should resemble the change a molecule undergoes when hydrogen is changed by deuterium. They studied several classical and nonclassical carbocations (along with neutral molecules), and the C-H bond being modified was that α to C^+ .

If, as is generally assumed, the Born-Oppenheimer approximation is valid, the electronic energy surface is the same for the hydrogen- and deuterium-containing molecules. The bond length at the minimum energy is the same for all isotopomers. Isotope effects arise from the differences in vibrational zero-point motion and energy on this surface. Bond lengths, measured with different physical methods, are different averages over this motion. The different average measures of bond length are affected by isotopic substitution (differently). It is only in this sense that bond lengths of isotopic molecules can be regarded as different. The intrinsic isotope shifts in the NMR can be considered as resulting from the differences in the averages of the chemical shift values over this vibrational motion. Since the form of the function of chemical shift versus distortion due to vibrational motion is not known, it is not clear how assumption of different bond lengths is related to chemical shifts.

The gross total charges and gross orbital charges of individual nuclei were plotted as a function of the C-H bond length.⁷¹ Both were found to be almost linear for small modifications of the bond distance. The plot of total charge against the C-H distance gave similar negative slopes for the carbon attached to the hydrogen being analyzed, that is, increased electron population as the bond shortens. This was predicted to produce increased shielding at that carbon, and hence in an isotope-induced upfield shift, in accord with experimental results.

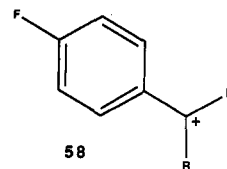
On the other hand, for the carbon β to the hydrogen (C^+), the slopes had a wide range of positive values. The wide range was interpreted as reflecting varying

degrees of electron demand, with the positive value meaning a deshielding of the β carbon nucleus as the C-H bond gets shorter. This should give as a result an isotope-induced downfield shift of C^+ . However this is experimentally observed only for classical carbocations, where hyperconjugation with a C-H bond is important. For nonclassical carbenium ions, a β deuterium causes a relatively large upfield shift, suggesting a different origin of the isotope effect.

In another study of the β -hydrogen isotope effect on trigonal carbons, Arrowsmith and Kresge found a linear relation between the isotope effect and the ^{13}C chemical shift of unsaturated carbons.⁷² However, the data for *tert*-butyl, *tert*-amyl and 1-methylcyclopentyl carbocations did not fit well in the correlation, perhaps as a result of the different conditions at which the NMR spectra were obtained. The observed results indicate that for an increase of the positive charge at the sp^2 carbon, the isotope effect becomes larger because hyperconjugation plays a more important role.

A smooth change of the isotope effect, from large downfield shifts for molecules needing hyperconjugative stabilization, to moderate upfield shifts for those cases in which hyperconjugation is not expected to be important, was also observed. This was interpreted as the simultaneous operation of two different effects of the isotope on the chemical shift. The first one causes an upfield shift and is only apparent in cases where hyperconjugation is not important. It was attributed to the smaller vibrational amplitude of the heavier system, which makes the C-D bond more shielding. The second effect, prominent in hyperconjugating systems, has also been attributed to bond shortening and its effect on the electron density of the carbon nuclei.⁷¹ Arrowsmith and Kresge, however, propose an additional mechanism in which bending vibrations are involved. The C-H bond has a greater vibrational amplitude than a C-D bond, and hence it is able to reach a more parallel situation when adjacent to a p orbital, giving a better hyperconjugative interaction. When the hydrogen is substituted by deuterium, the net result is a downfield isotope shift.

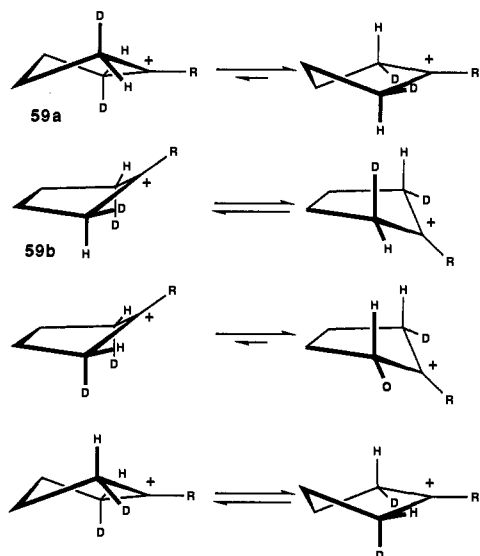
Earlier studies on (*p*-fluorophenyl)carbenium ions showed that deuteration β to the cationic center originates changes in the chemical shift of fluorine which are very similar to β -deuterium kinetic and equilibrium isotope effects of typical carbocations.⁷³ Recently, Forsyth et al.⁷⁴ prepared a series of (*p*-fluorophenyl)carbenium ions (58) with several alkyl substituents at the benzylic carbon. One of the substituents was



deuterium-labeled at the β - or γ -positions. It was observed that β -substitution causes a downfield shift of the ^{19}F peak, while γ -deuteration generates an upfield shift, apparently increasing the electron-donating character of the alkyl group. This γ -inverse isotope effect on the chemical shift of fluorine is remarkably analogous to some observed γ -kinetic isotope effects of carbocations.

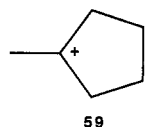
Experimental kinetic and equilibrium isotope effects indicate that a cationic center typically weakens force

SCHEME VIII



constants for a β C–H bond, while the opposite is true for the γ C–H bond. Forsyth suggests that because the stabilizing effect of an alkyl group on a carbocation is given by a contribution of hyperconjugative, inductive, and field effects a shorter C–D bond γ to the cationic center enhances electron-donating interactions (by inductive effect). On the other hand, β -deuteration opposes the natural tendency of the β C–H bond to become longer, reducing the electron-donating interaction (by hyperconjugation) of the alkyl group. In other words the differences in electronic densities between isotopomers are caused by changes in the averaged vibrational structure within the same anharmonic energy surface. Additional results also suggested a dependence of the isotope-induced shifts on conformational factors.

It is assumed in many studies that isotope effects for typical multiply labeled carbocations should be additive. However, for conformationally mobile species, perturbation of the equilibrium of the rotamers by the isotope can result in nonadditivity. The additivity properties in multiple isotopic substitution can then be used to determine the preferred conformations in cationic systems. Following this methodology, the 1-methylcyclopentyl cation (59) was found to prefer a twisted conformation 59a over an envelope 59b or a planar ring.⁷⁵ For this system, several deuterated isotopomers



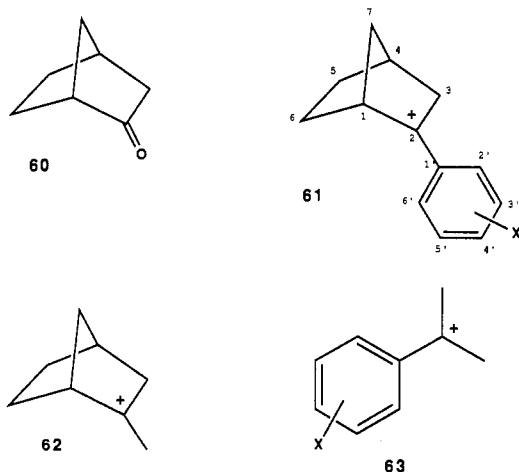
were studied. It was found that sequential deuteration at positions 2 and/or 5 did not have an additive effect on the chemical shift of the cationic carbon, ruling out the planar conformation. The envelope was discarded on the grounds of the isotope-induced shifts observed for the 2,5-dideuterio *cis* and *trans* isotopomers. The shift for *cis*-2,5-dideuterio was found to be almost half of that for 2,2,5,5-tetradeuterio, while *trans*-2,5-dideuterio produced a much smaller shift. This can only be explained by a twist conformer (Scheme VIII).

Another interesting observation, that has been also noticed for equilibrium isotope effects, was that the

β -CD₂-R isotope effect on the chemical shift of C⁺ was 2.9 times stronger than that for a β -CD₃. From a model based on the hyperconjugation dependence on $\cos^2 \theta$ (where θ is the dihedral angle between the bond involved in the hyperconjugation and the p orbital) it would be expected that $\Delta(\text{CD}_2)/\Delta(\text{CD}_3) \leq 1$. An inverse isotope effect of the C–D bond at 90° with the p orbital is highly unlikely, for it would have to be very large to account for the upfield shift. The observed results imply that, somehow, hyperconjugation with an endocyclic methylene is stronger than with an exocyclic methyl.

To further explore this point, MINDO/3 calculations were carried out on the 1-methylcyclopentyl cation. To simulate the effect of deuteration, the involved C–H bonds were shortened, and their effect on the electronic charge at C⁺ was compared against the charge calculated for the nondeuterated ion (Δq). In the MINDO/3 energy surface the lowest energy conformer is a slightly bent envelope. Nevertheless, both this envelope and a planar conformation did not show any evidence of greater methylene than methyl interaction. On the other hand, the twist conformer, although higher in energy (at least for MINDO/3), did show a different pattern. The *trans*-axial C–H has a much better interaction with the cationic center, showing a strong tendency toward hyperconjugative lengthening and bridging. For a partially bridged twist conformation, the ratio $\Delta q(\text{CD}_2)/\Delta q(\text{CD}_3)$ was calculated to be 2.3, in close agreement to the experimental isotope shift of 2.9. It is finally suggested that a weakly H-bridged twist structure is the true energy minimum conformer for the 1-methylcyclopentyl cation.

In another very interesting study, ¹³C isotope induced shifts were measured in 2-norbornanone (60), 2-aryl-2-norbornyl (61), 2-methyl-2-norbornyl (62), and 2-aryl-2-propyl (63) cations.⁷⁶ For the norbornyl systems, the



exo-3-deuterio-, *endo*-3-deuterio-, and 3,3-dideuterio-substituted ions were used. It was found that the *exo* and *endo* isotope effects are additive within experimental error; their effect, however, was different. This was expected because these hydrogens are diastereotopic. In addition, the *exo* hydrogen is better aligned with the p orbital at C₂, having stronger hyperconjugative interactions. For 62, a process was observed which interchanges deuterium between *exo* and *endo* positions, leading to an equilibrium mixture in which *endo*-deuterium is predominant. 2D NMR experiments

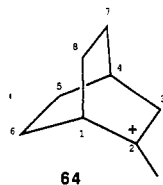
showed exchange between C_1-C_6 and C_5-C_7 . The same scrambling was observed for the 2-aryl-2-norbornyl cations with the most electron-withdrawing substituents, $4'-CF_3$ and $3',5'-(CF_3)_2$.⁷⁷

For the 2-aryl-2-norbornyl cations **61**, an *endo*-deuterium at C_3 produces an upfield shift of C_2 , while the *exo* causes a downfield shift. This seems to indicate that the *endo*-deuterium is producing an inductive effect which is not counterbalanced by hyperconjugative interaction. Additionally, only the *exo*-deuterium induces downfield shifts at the ortho and para positions of the aryl ring. However, no isotope shifts were observed for the $4'-CF_3$ and $3',5'-(CF_3)_2$ derivatives, perhaps as a result of reduced charge delocalization of the cationic center with electron-withdrawing rings.

A plot of the isotope shifts at C^+ against σ^{C^+} for the 2-aryl-2-propyl cations **63** (fully deuteriated at the methyl positions) gives a straight line. In contrast, for the 2-aryl-2-norbornyl cations a plot of the 3,3-dideuterio, *exo*-3-dideuterio, and *endo*-3-dideuterio gives a linear correlation only if the data for $4'-CF_3$ and $3',5'-(CF_3)_2$ is not included. For these derivatives, the deviation is upfield for all three plots, the *exo* shift being almost twice as large as that for the *endo* deuterium. This indicates that, for the most electron-withdrawing substituents, the isotope is perturbing a three-center, two-electron bond, shifting it toward enhanced σ -bridging.⁷⁸ To explain this in terms of the change induced in the vibrationally averaged structure resulting from deuterium substitution, the authors suggest "...that the isotope shift will start to show behavior characteristic of σ -bridging as soon as the energy barrier for the bending motion along the bridging coordinate [that involving $C_2-C_1-C_6$] is lowered sufficiently [as a result of increased electron demand at C_2] that the vibration occurs in a shallow potential well, even if the vibrationally averaged structure is only slightly bridged".⁷⁸

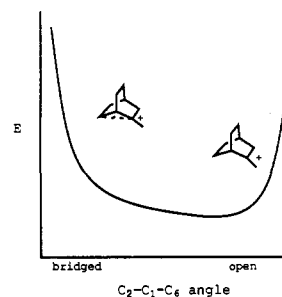
For **62**, both *exo* and *endo* deuteriation at C_3 give large upfield isotope shifts, the effects of the *exo* deuterium being almost twice as large as that for the *endo* (1.64 vs 0.87 ppm). This shift is one order of magnitude larger than the upfield shift observed for the $3',5'$ -bis-(trifluoromethyl)aryl derivative. Because the ion is more electron demanding, it should have a stronger tendency toward a bridged structure, hence the larger isotope effect.

On the basis of the chemical shift of the cationic carbon, the 2-methyl-2-bicyclo[2.2.2]octyl (**64**) cation was considered as classical while, on the same grounds, the 2-methyl-2-bicyclo[2.2.1]heptyl (2-methyl-2-norbornyl)cation (**62**) is better represented as a partially bridged structure.⁷⁹ Nonetheless, both display a similar



pattern of isotope-induced shifts.⁸⁰ Deuteriation at C_3 or at the methyl induces exceptionally large upfield shifts at C^+ , and large downfield shifts at C_1 .⁸¹ In addition, the carbon attached to C_2 (either CH_3 or C_3), with no deuterium, suffers a substantial upfield shift.

SCHEME IX



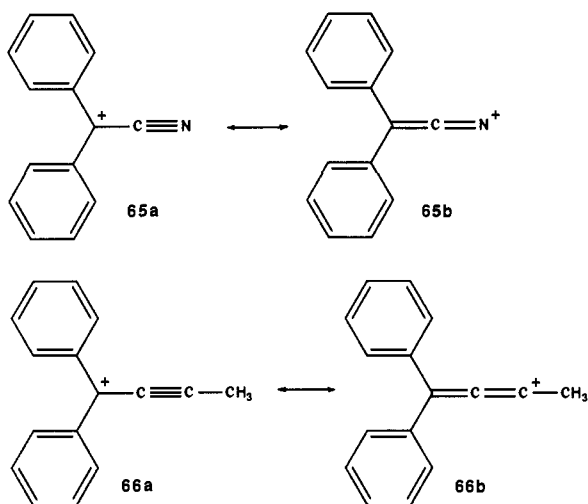
This is consistent with perturbation of a σ -delocalized structure toward greater σ -delocalization, increasing the electron density at C^+ , and decreasing it at C_1 . An additional piece of evidence is the fact that both *endo* or *exo* deuteriation at C_6 in **64** produce a downfield isotope shift at C^+ compatible with decreased σ donation. It was also observed that there is a small temperature dependence of both, the isotope shifts and chemical shifts for the 2-methyl-2-bicyclo[2.2.2]octyl cation.

It can be seen that there is an apparent contradiction in what is concluded for **64**. To explain this, several possibilities were analyzed, and some of them were discarded. The temperature-dependent shifts agree with an equilibrium between two very similar structures, one of them the classical ion, and the other, an enantiomeric mixture of a partially bridged form in which either C_3 or C_8 are forming the bridge. This bridged structure was estimated to be only slightly higher in energy than the open ion. The authors suggest that instead of an equilibrium the observed results can be explained by proposing that both structures are two points on the same continuous flat energy surface for the coordinate associated with bridging, that involving $C_2-C_1-C_6$ bending. Because of its anharmonicity (Scheme IX), a change in temperature and/or isotopic substitution gives a different vibrationally averaged structure, and hence a change in the average electronic density. The slight temperature dependence of other chemical shifts is also in agreement with this suggestion.

The isotope shift data for **62** is also consistent with a more bridged structure resulting from deuteriation. On the other hand, the dependence of these shifts on temperature is different than in **64**, suggesting two possibilities: (a) That in the flat energy surface the bridged structure is slightly more stable than the open ion, or (b) the energy surface of the $C_2-C_1-C_6$ bending is more harmonic, and a change in temperature would have a smaller effect. One must remember, however, that the chemical shift of C_2 suggests a more bridged structure.

A mixture of all 10 possible ring monodeuteriated isotopomers of the 2-methyl-2-norbornyl cation **62** was observed with ^{13}C NMR spectroscopy under superacidic conditions at 173 K.⁸² For each of them, a different resonance of the cationic center is observed, evidencing a different isotope effect at each position. There is a difference of approximately 3 ppm between the lowest and highest induced shifts. It was not possible to assign all these resonances to the corresponding isotopomers, because of the rearrangement processes that occur even at 143 K. The largest downfield shift, 1.45 ppm, was associated with the *exo*-6-deuterio isotopomer, while the

SCHEME X



largest highfield shift (1.64 ppm) was assigned to deuteration at the 3-endo position.

The second largest isotope-induced shift was tentatively assigned to the *endo*-6-deuterio. Its value (0.91 ppm) is almost half of that for the *exo*-6-deuterio. This seems to be in agreement with a model in which the electrons of the C₆-C_{exo} bond play an important role in the stabilization of the ion, through interaction of the backside lobe of the bonding orbital with the empty p orbital at the cationic center.⁸³ It is concluded that a *exo*-6-deuterium shifts the bridged structure toward a more open ion, giving a more deshielded C⁺, while deuteration at position 3 gives as a result a more bridged structure and a more shielded cationic carbon.

7. Coupling Constants in Carbocations

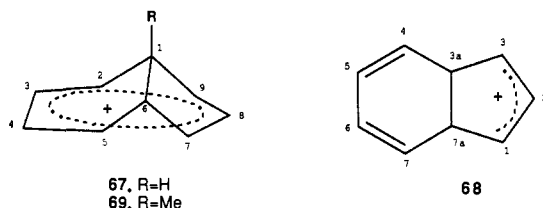
The values of $^1J_{C-C}$'s have been correlated with the hybridization of the atomic orbitals forming the C-C bond, hence it can be used to estimate the bond order between two carbons in structurally related compounds; larger coupling constants meaning higher bond orders.

Solvolytic studies⁸⁴ have shown that a cyano group bonded to a cationic carbon stabilizes it through resonance interactions, despite the fact of the strong inductive electron-withdrawing effect. This is supported by ¹⁵N NMR spectroscopy in cyanodiarylmethyl cations (65), in which electron-donor substituents shield both the cyano nitrogen and C⁺.⁸⁵ Because the structurally related 1,1-diaryl-2-butynyl cations (66) should behave in a similar manner (Scheme X), Olah and co-workers decided to study the effect of substituents on the coupling constants between the cationic center and the α carbons in both systems.⁸⁶ They expected to find evidence of a change in bond orders, as the contribution of the resonance forms becomes more or less important.

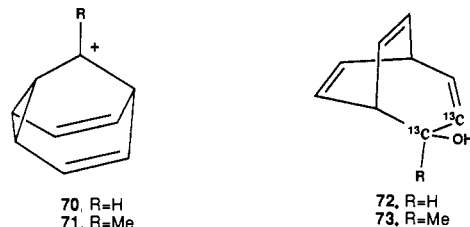
The coupling constants were measured in ions ¹³C enriched at the cationic carbon; the substituents studied were H, *p*-Me, and *p*-MeO. For 66, electron-donating substituents shield C₁ and C₃ in a very similar way as in the cyanodiarylmethyl cations, evidencing decreased participation of the allenyl resonance structure 66b. Regarding the coupling constants for the cyanodiarylmethyl cations, J_{C^+-CN} remains practically constant (76.5 \pm 1 Hz) regardless of the substituents. However, this value is more than 11 Hz larger than that observed in the parent cyanohydrins for the same carbons. This

large difference between the neutral and cationic structures is not observed in classical cations lacking π -delocalization and may be interpreted as an increased double bond character between the involved carbons. The same trend is observed for the butynyl cations for which J_{C-C} has an almost constant value of 90.0 Hz, approximately 11 Hz higher than the corresponding alcohols. On the other hand, for both systems $J_{C^+-C_{ipso}}$ increases with the electron-donor character of the substituents. It is concluded that, for these systems, a substituent-induced change in the bond orders is reflected in the $J_{C^+-C_{ipso}}$, while $J_{C^+-C_{\alpha}}$ is not affected.

Jonsäll and Ahlberg made use of $^1J_{C-C}$'s as a probe of homoaromaticity in the 1,4-bishomotropylium ion 67.⁸⁷ NMR spectroscopy in superacid supports its aromatic character, while solvolytic studies suggest that it has the planar dihydroindenyl structure 68 instead.⁸⁸ In addition ab initio (STO-3G) and semiempirical calculations find both structures to be energy minima.⁸⁹



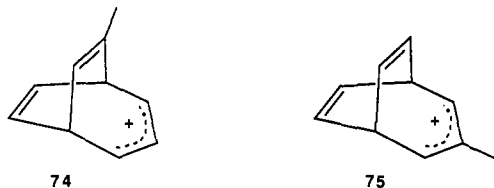
¹³C-Dilabeled 67 and the 1-methyl-1,4-bishomotropylium ion (69) were obtained by rearrangement, in superacid, of the corresponding 9-barbaralyl cations 70 and 71 which in turn were generated by ionization of the [2,3-¹³C₂]bicyclo[3.2.2]nona-3,6,8-trien-2-ol (72) and the 2-methyl derivative 73. While at the barbaralyl



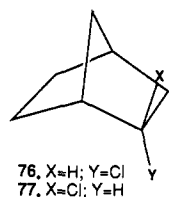
stage, the labeled carbons scrambled throughout the molecule, making it possible to get almost all the coupling constants ($^1J_{C1-C6}$ cannot be measured in the parent ion because of symmetry). The $^1J_{C-C}$ and $^1J_{C-H}$ values thus obtained were discussed in terms of what would be expected for a bishomotropylium or a dihydroindenyl structures. They were also compared with experimental values of model compounds, and discussed in terms of the results of MINDO/3 and MINDO semiempirical MO calculations. The coupling constants at the bridgehead positions are consistent with partial formation of two three-membered rings, the bridgehead carbons being almost sp² hybridized. Estimation of the s character of the carbon hybrids from the coupling constants, also supports a bishomoaromatic structure. The estimated s character at the homoaromatic bonds (C₂-C₉, C₅-C₇) is 0.1. ¹³C chemical shift additivities give a difference of 192 ppm between 67 and dihydroindene, the parent hydrocarbon. This strongly indicates that the structure of the ion in superacid is not 68.

Regarding the 9-barbaralyl cations, several interesting results were obtained. Chemical shift additivities clearly place them among the classical ions ($\Delta\delta = 457$ ppm between 70 and the corresponding hydrocarbon).

The double ^{13}C labeling allowed the identification of three different degenerate scrambling processes for 71, one of them not previously observed. The first rearrangement occurs at $-137\text{ }^\circ\text{C}$ upon addition of the corresponding alcohol to superacid, and it interchanges only C_1 and C_5 . This process is believed to take place through a series of ring-opening and ring-closure steps. In the second, at $-131\text{ }^\circ\text{C}$, the label is scrambled at positions 2, 4, 6, and 8, and it is proposed to occur via reversible opening to the 6-methylbicyclo[3.2.2]nonatrienyl cation (74), with a ΔG^\ddagger of 10.4 kcal/mol. Also at $-131\text{ }^\circ\text{C}$ another process was observed which scrambles the label to C_2 , C_3 , C_4 , C_6 , C_7 , and C_8 . It is suggested that this rearrangement occurs via ring opening of 71 to the 3-methylbicyclo[3.2.2]nonatrienyl cation 75.



Using a technique similar to that just mentioned, Jarret and Saunders were able to determine all of the $^1J_{\text{C-C}}$'s in the *endo*- and *exo*-norbornyl chlorides (76 and 77, respectively), using as starting material [2,3- $^{13}\text{C}_2$] 2-norbornyl chloride.⁹⁰ Treatment with a catalytic



amount of SnCl_4 in nitrobenzene, eventually led to complete scrambling of the labeled carbons, through ionization and recombination of the ions. After several days, the equilibrium mixture contains a 5:1 mixture of *exo* and *endo* isomers. The changes of the NMR spectrum as a function of time, that is, the order in which isotopomers appear, can be completely explained with the already recognized rearrangement processes, namely, Wagner-Meerwein 6,2-hydride and 3,2-hydride shifts. Rune-Kutta simulation of this rearrangements, along with the NMR data, suggest that if a hypothetical rearrangement of the norbornyl to a norpinyl cation is occurring simultaneously with the other processes, it is less than 1/20 as fast as the 3,2-hydride shift at room temperature. The coupling constants are found to be in the range of normal sp^3 C-C bonds. Several long-range coupling constants were obtained as well.

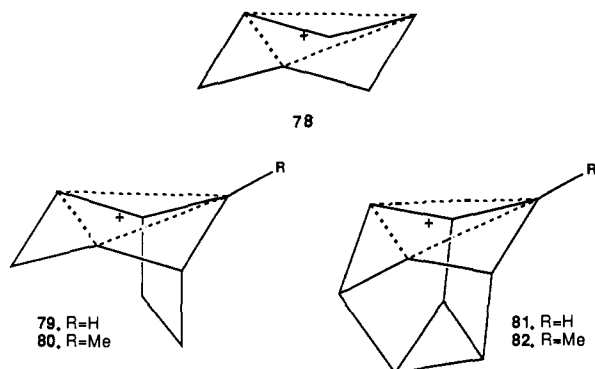
Some time ago, while investigating the factors that affect one-bond C-H coupling constants in carbocations, Kelly and Brown⁹¹ developed an empirical equation, which relates the difference (ΔJ) between the $^1J_{\text{C-H}}$ of the C-H bond adjacent to a cationic center and the coupling constant in the corresponding ketone with the dihedral angle between the p orbital and the C-H bond in the cation.

$$\Delta J = A - B \cos^2 \theta$$

For classical cations, the maximum value ΔJ is expected to take occurs when $\theta = 90^\circ$, that is, $\Delta J = A$, which has a value of 22.5 Hz. A larger value can be

taken as an indication of σ -bridging, due to the increased s character of the C-H bond. Kelly and co-workers used this approach to assess the nonclassical character of several trishomocyclopropenium cations.⁹² The systems that were studied had been previously described as nonclassical on the grounds of their behavior under both solvolytic, and superacidic conditions.

It was found that for the cations bicyclo[3.1.0]hex-3-yl (78), tricyclo[3.2.1.0^{2,4}]oct-8-yl (79) and its 8-methyl derivative 80, and pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-9-yl (81) and its 9-methyl derivative 82 the $^1J_{\text{C-H}}$ at the carbons forming part of the homoaromatic system, were substantially large (21–32 Hz). In addition, the C-H



coupling constant at the methylenes in between the bridging carbons has a high value as well (18–27 Hz). From these results, it is concluded that these carbocations are true $\pi\sigma$ -bridged nonclassical ions.

8. Equilibrium Isotope Effects⁹³

At $-65\text{ }^\circ\text{C}$ the rearrangement processes in the 2-norbornyl cation 1 are fast enough to give a three-signal ^{13}C NMR spectrum corresponding to $\text{C}_{1,2,6}$, $\text{C}_{3,5,7}$, and C_4 .⁹⁴ On the other hand, at $-155\text{ }^\circ\text{C}$ the Wagner-Meerwein rearrangement is still fast, while the 6,2-hydride shift is slow and the 3,2-hydride shift is completely suppressed. This gives rise to a five-line NMR spectrum at this temperature with peaks corresponding to $\text{C}_{1,2}$, C_6 , $\text{C}_{3,7}$, and C_4 .

Jarret and Saunders studied the ^{13}C equilibrium isotope effect in the 2-norbornyl cation by ionizing the dilabeled [2,3- $^{13}\text{C}_2$]norborn-2-yl chloride⁹⁰ and allowing the resulting ion to completely scramble the labeled carbons.⁹⁵ As a result, several averaged coupling constants could be measured. It was determined that none of the C-C coupling constants in the ion is larger than 50 Hz. In addition, because the labels can be found at different positions in the isotopomers, several signals can be seen for the same carbons. For example, at $-65\text{ }^\circ\text{C}$, C_4 produces a singlet for molecules in which the second label is at carbons 1, 2, or 6 (nonadjacent positions) and a doublet for those molecules in which the second label is at carbons 3, 5, or 7. Similarly, the averaged signal corresponding to $\text{C}_{3,5,7}$ contains two doublets and two singlets, whose distribution is not symmetric about a single point. At this temperature, the peak corresponding to $\text{C}_{1,2,6}$ is not resolved.

The asymmetry of the $\text{C}_{3,5,7}$ signal, that is, displacement from the expected frequency, clearly indicates a ^{12}C - ^{13}C equilibrium isotope effect. By considering the magnitude of the shifts, along with all possible equilibrium processes for the involved carbons, it was pos-

sible to evaluate two $^{12}\text{C}/^{13}\text{C}$ isotope effects at different positions of the ion, the values being $K_{3,5-7} = 1.010$ ($\Delta G = 4.1$ cal/mol), and $K_{1,2-6} = 1.039$ ($\Delta G = 15.8$ cal/mol) the largest reported equilibrium ^{13}C isotope effect. The first value corresponds to a small preference of ^{12}C to occupy positions 3 and 7, rather than 5. On the other hand, there is a very strong preference of ^{12}C to occupy the pentacoordinated C_6 position. Because of the known preference of heavier isotopes to reside at sites involved with stronger bonds, these results are consistent with the idea that the formation of five partial bonds gives a total bond strength which is less than that of a tetravalent site.

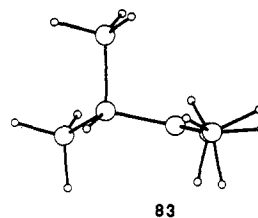
It is well known that from nortricycyl or norbornenyl precursors, the same stable carbocation is obtained. However, although available data strongly pointed toward a localized nortricycyl structure 48, it was not possible to rule out an equilibrium between the nortricycyl and two enantiomeric norbornenyl cations. In order to get insight into this problem, Saunders and co-workers⁶³ applied the isotopic perturbation method to the nortricycyl–norbornenyl cation.

A mixture of norbornenyl and nortricycyl chlorides dideuterated at C_3 was ionized, and a ^{13}C NMR spectrum was taken at -110 °C. The latter showed a very small splitting (0.7 ppm) of the $\text{C}_{1,2}$ resonance, which displayed no temperature dependence. This is clearly in contrast to the much larger and temperature-dependent splitting expected for an equilibrium involving norbornenyl cations. The small splitting can be very well interpreted as an intrinsic effect of the deuteriums at C_3 , on the chemical shift of C_2 .

In addition, several rearrangement processes were detected. By using ^2H NMR it was observed that, for the C_3 -dideuterated ion, the *exo*-deuterium scrambles to all other positions, while the *endo* scrambles only around 0 °C. Magnetization transfer was also observed to occur at -35 °C, between the protons at C_1 , C_4 , and C_5 . ^{13}C NMR of the ion ^{13}C -dilabeled at C_2 and C_3 shows, at -70 °C, scrambling of C_2 to positions 4 and 5. Above -50 °C total scrambling is observed, it is possible to obtain all $^1J_{\text{C-C}}$'s for the ion. The experimental results suggest the presence of three degenerate processes. The fastest step involves skeletal rearrangement with no hydride shift. All evidence points to a reversible rearrangement of the nortricycyl to the bicyclo[3.1.1]heptenyl cation (49). The process is fast even at -70 °C. The second rearrangement occurs readily at -50 °C and involves a 1,2-hydride shift. Finally, at 0 °C, a 1,3-hydride shift takes place and, at this temperature, all hydrogens and carbons scramble completely.

The experimental $^1J_{\text{C-C}}$'s and ab initio quantum mechanical calculations suggest that the C_5 – C_6 bond contains a substantial amount of double bond character, while the C_1 – C_6 and C_2 – C_6 bonds are quite long. This seems consistent with considerable delocalization of the positive charge between the two adjacent cyclopropane bonds and the cationic center.

Earlier ^1H NMR studies of the 2,3-dimethyl-2-butyl cation (83) indicated nonadditive equilibrium isotope effects on multiple deuterium substitution.⁹⁶ Saunders and Cline⁹⁷ reexamined this system using both theoretical and experimental approaches in order to investigate the origin of this nonadditivity.



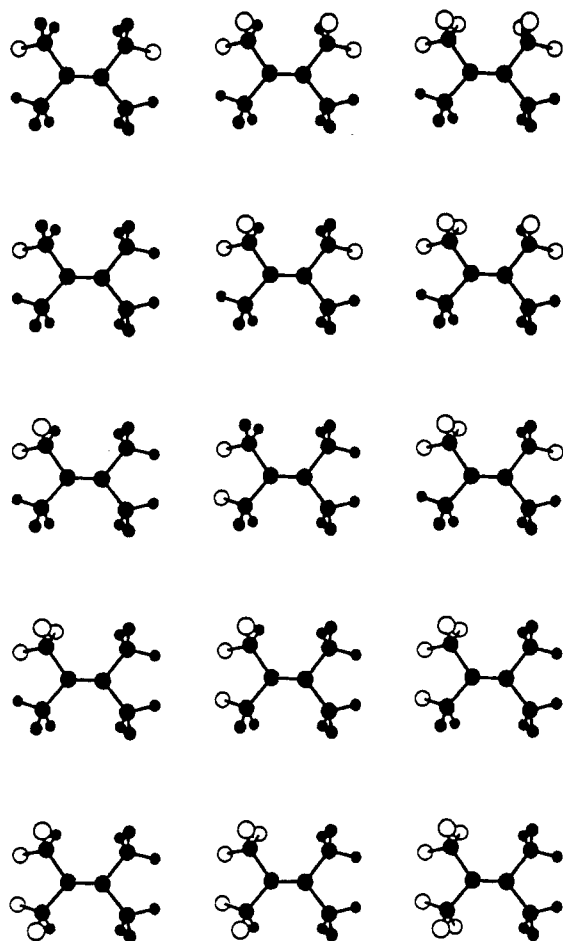
The geometry of the ion was optimized at the 3-21G and 6-31G* levels of theory. The final structure was found to be asymmetric and bond lengths and angles suggested strong hyperconjugative effects. One hydrogen in each of the methyls α to the cationic center is almost parallel to the p orbital, while another hydrogen in each of these methyls is practically orthogonal to the p orbital. In addition, one of the β methyls is also parallel to the p orbital, and its hydrogens show small hyperconjugative effects as well. From the theoretical structure it was expected to find a conformational preference of the heavier isotopes (^2H and ^{13}C) on those sites less involved in hyperconjugation.

The theoretical values of the equilibrium isotope effect, on the degenerate 1,2-hydride shift, were calculated from the Cartesian force constant matrix (frequency analysis at the 3-21G level), with use of the program QUIVER.²⁵ This program first calculates the vibrational frequencies of the desired isotopomers and from them, the reduced isotopic partition function ratios, $(s^2/s^1)f$. Because of the asymmetry of the theoretical structure, for each isotopomer all possible conformations of the isotope had to be considered in the calculation. From the calculated $(s^2/s^1)f$'s it is possible to obtain the theoretical equilibrium constant for any isotopomer or the predicted population of any given conformer within an isotopomer.

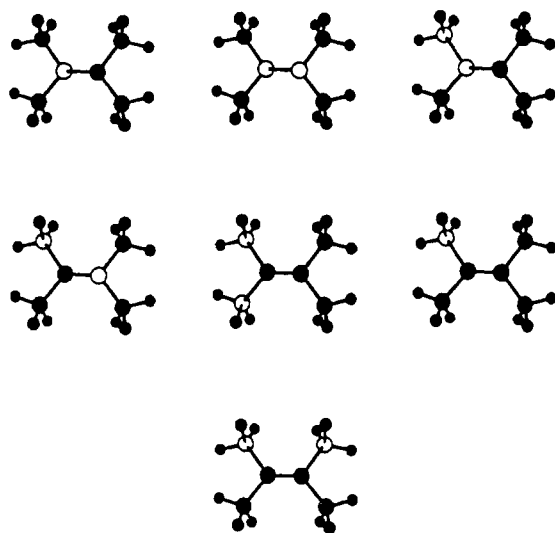
A mixture of mono and polydeuterated 2,3-dimethyl-2-butyl cations, with deuteration restricted to no more than two methyls, was prepared from a mixture of polydeuterated alcohols ^{13}C enriched at the hydroxyl carbon. At equilibrium, the mixture contains 15 isotopomers (Scheme XI). Three of them give a single line for the averaged C^+ methine carbon because of symmetrical deuteration. The other 12 can be arranged in groups, according to the excess number of deuteriums on one side over the other. From the splittings due to the isotope effects and a plot of K_{eq} vs $1/T$, it is readily observed that multiple deuteration produces nonadditive changes in the equilibrium constant. On the other hand, it is possible to predict the isotope effects by using additivity by group, that is, by using the values of the K_{eq} 's for the simple mono-, di-, and trideuterio-methyl groups as starting points. This means that deuteriums on one methyl produce isotope effects which are almost independent from those in other methyls.

The nonadditivity of the isotope effects, within a single methyl, was attributed to (a) intrinsic nonadditivity, which comes from the change of vibrational motions caused by multiple deuterium substitution and (b) conformational nonadditivity, that is, a preference of the heavier isotope for a specific conformation. The equilibrium constants obtained with QUIVER include both effects, but it is possible to calculate the conformational isotope effects from the conformational populations, also obtained with QUIVER. The almost exact agreement between the equilibrium constants calculated in both ways suggest that conformational preference is

SCHEME XI



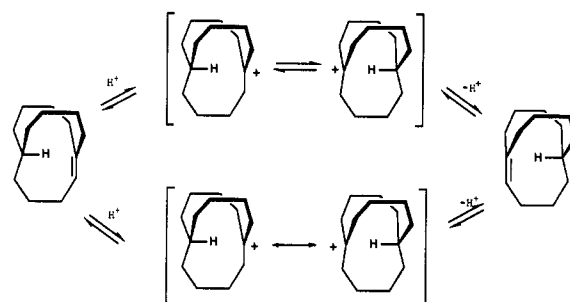
SCHEME XII



the main source of the nonadditivity in this ion.

The ^{13}C -dilabeled ion was also prepared and scrambled, generating all possible isotopomers (Scheme XII). The NMR spectra show the participation of primary and secondary isotope effects in which ^{13}C prefers to be at the cationic center rather than at the methine position, or on a methyl attached to the cationic carbon rather than away from it. Although the theoretical approach suggests a small nonadditivity of the isotope effect for the isopropyl methyls, experimentally it was not possible to detect any conformational nonadditivity.

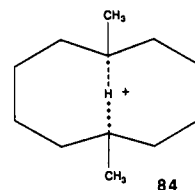
SCHEME XIII



In general, the agreement between theory and experiment was found to be very good, although higher level quantum mechanics calculations might be required to fully reproduce the effects of hyperconjugation on the vibrational frequencies of the ion.

9. μ -Hydrido-Bridged Carbocations

Previous studies have shown that in the 1,6-dimethyl-1-cyclodecyl cation (84), a transannular C-H-C three-center, two-electron bond is formed.⁷ However, the ion is not stable above -70°C . Its instability can be attributed to both the conformational mobility of the system and the fact that rearrangement processes to give more stable species can easily occur.



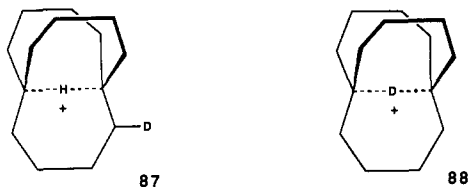
McMurry and co-workers reasoned that, in order to have a stable μ -hydrido-bridged cation, it is necessary to have a rigid structure, with the hydrogen involved in that bond "trapped" within the appropriate geometry. Thus, they chose to generate the *in*-bicyclo-[4.4.4]-1-tetradecyl cation (85)^{9b} and, as its precursor, they synthesized and characterized the *in*-bicyclo-[4.4.4]-1-tetradecene (86).



At first they thought that the best way to generate the ion would be through ionization of the corresponding chloride, which in turn would be obtained by addition of HCl to the olefin. However, no reaction was detected on treatment of the olefin with dry HCl in a variety of solvents. Observation of the reaction mixtures using ^1H NMR showed that in polar solvents a new species was formed with a signal corresponding to a single proton at -3.46 ppm. In cyclohexane, they noticed that the tertiary chloride was formed almost immediately, but it went back to the olefin on solvent removal. In addition, when the olefin was treated with CF_3COOD , the recovered olefin had incorporated deuterium at all 11 positions adjacent to both bridgehead carbons. This can be explained only if at some point of the process the bridgehead positions become equiv-

alent, which can occur by assuming the formation of either a nonclassical species with a three-center, two-electron bond, or a rapid equilibrium between two classical carbocations in which hydride transfer occurs (Scheme XIII).

The cation was found to be indefinitely stable at room temperature. Its ^{13}C NMR spectrum contains only three signals. The bridgehead carbons appear at 139.3 ppm, far upfield of what would be expected for a classical cation. In addition, the corresponding $J_{\text{C-H}} = 47$ Hz denotes decreased spin density at the C-H bond. These results strongly suggest that the observed cation is nonclassical. In order to rule out the equilibrium process between two classical cations, additional NMR experiments were carried out. In the first of them, Saunderson's isotopic perturbation method was used. The ^{13}C NMR of the deuterated species 87 showed a splitting of 0.8 ppm (at -92 °C) of the resonance corresponding to the bridgehead carbons, with a very small temperature dependence (the splitting is 0.2 ppm at 0 °C).⁹⁹ In the second experiment, the test of Altman and Forsén was employed.¹⁰⁰ The ^2H NMR of the deuterated cation 88 was obtained. The chemical shift of the bridged deuterium was -3.36 ppm, 0.10 ppm downfield of its hydrogen counterpart.¹⁰¹ These results clearly indicate a nonclassical structure with a three-center, two-electron bond.

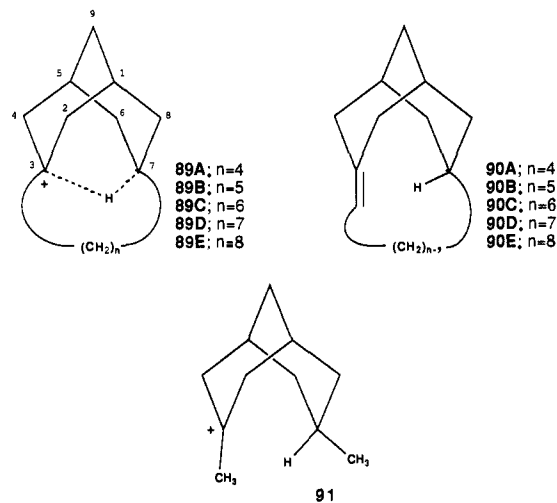


Further information was obtained by using different methods. IR spectroscopy of a solution of 85 showed a strong band at 2113 cm^{-1} which shifted to 1558 cm^{-1} on isotopic substitution (IR of 88). The band was assigned to asymmetric stretch within the D_3 symmetry. By assuming that the C-H-C bond behaves as a classical three-body oscillator, the corresponding force constant k was calculated to be 1.26×10^5 dyn/cm. The same calculation on the C-D-C oscillator gave an almost equal result, 1.32×10^5 dyn/cm. These values are more than 3 times smaller than those found for a normal C-H bond. A quantitative measure of the stability of the ion was made by determining its acidity-basicity properties. The results showed that it is as weak an acid as acetic acid, while the corresponding olefin is as basic as acetate ion. Semiempirical (AM1) and ab initio (6-31G) found a single minimum in the potential surface of the ion, in agreement with experimental results.

Looking for a better understanding of the μ -hydrido-bridged cations, Sorensen and Whitworth studied the influence of the distance between the two carbon centers on the nature of the three-center, two-electron bond.¹⁰² For this purpose, they used the tricyclic system 89, based on the 3-bicyclo[3.3.1]nonane. The cationic center would then be generated at C_3 , while the effect of varying the hydrocarbon between C_3 and C_7 would be studied. For a long chain, the distance between C_3 and C_7 is expected to be too long for bridging. On the other hand, by systematically decreasing the number of carbons in this chain, one would expect to reduce this distance and hence to change the nature of the inter-

action between the three atomic centers.

As precursors of cations 89B-89E, the corresponding olefins 90 were used. It was not possible to synthesize 90A. As reference, the unconstrained 3,exo-7-dimethyl-3-bicyclo[3.3.1]nonyl cation (91) was first generated. The NMR spectra suggest the presence of two

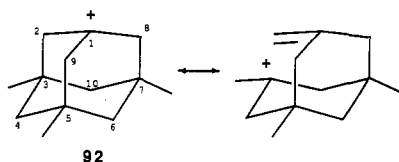


classical structures in equilibrium, with a $\Delta G^\ddagger = 3.5 \pm 0.5$ kcal/mol. Because of this very small barrier, it was not possible to "freeze" the hydride interchange in the range of temperatures in which the spectra were taken. The chemical shift of the hydrogen at C_7 is 0.30 ppm; it is found at high field, but not as high as would be expected for a μ -bridged hydrogen. MINDO/3 calculations also give a classical cation structure as the energy minimum. The interchanging hydrogen is calculated to have a slightly negative charge (-0.07), perhaps as a result of polarization of the C-H bond by C^+ .

89E was generated at -80 °C in $\text{FSO}_3\text{H-SbF}_5/\text{SO}_2\text{ClF}$, being stable below -20 °C. At -100 °C, the ^{13}C NMR spectrum shows a peak at 324.8 ppm, characteristic of C^+ in a classical tertiary carbocation. In addition, the chemical shift of H_7 was 0.07 ppm. Further evidence was found that for this cation, the hydride exchange can only occur through a conformational change in the $-(\text{CH}_2)_5-$ hydrocarbon chain. This process has a somewhat high energy barrier, allowing the observation of separate signals for C_7 and C_3 . 89D shows similar behavior. It is stable below -10 °C in $\text{FSO}_3\text{H-SbF}_5/\text{SO}_2\text{ClF}$. At -112 °C, C^+ has a chemical shift of 296.5 ppm, upfield of the corresponding signal in 89E; H_7 appears at -1.46 ppm. These chemical shifts can be interpreted as evidencing the onset of bridging. MINDO/3 calculations for the lowest energy conformers of 89E and 89D gave as a result classical structures, in agreement with the experimental results. The charge at H_7 is -0.109 for 89E and -0.111 for 89D.

89C could be prepared in $\text{FSO}_3\text{H/TFA}$. It is stable for several days at room temperature. The chemical shifts of H_7 (-4.26 ppm at -10 °C) is characteristic of a μ -hydrido bridge. The fact that this chemical shift is temperature dependent ($\delta -4.56$ at -105 °C) was interpreted by the authors as indicative of the presence of two bridged cations, one with a symmetrical bridge (minor species) and the other (major species) with the bridge being less symmetrical. 89B is completely stable in TFA at 25 °C. It is even stable in TFA diluted with water. The signal corresponding to the bridging hydrogen is found at 5.64 ppm, and it is unaffected by

SCHEME XIV



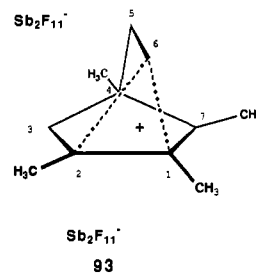
temperature changes, suggesting the presence of a single cation structure. There is, however, evidence of a conformational equilibrium at the hydrocarbon chain between slightly unsymmetrical conformers. In TFA/D₂O, **89B** exchanges the axial protons of the [3.3.1]nonane ring and all four hydrogens of the hydrocarbon chain that are adjacent to the bridgehead positions. MINDO/3 calculations on **89C** find the lowest energy structure to be a classical cation. The lowest symmetrically bridged structure is calculated to lie 5.1 kcal/mol above in energy. On the other hand, for **89B** the lowest energy structure is a μ -H-bridged cation, but an unsymmetrically μ -H-bridged structure was found to be only 0.45 kcal/mol higher in energy. As can be seen, the semiempirical calculations on **89B** and **89C** do not agree very well with the experimental results. For the authors, MINDO/3 underestimates the strength of the C-H-C bridging.

It is observed that in going from **89E** to **89B** the cations become weaker acids, and the corresponding alkane precursors become stronger bases. For Sorensen and Whitworth this tendency is not due to the μ -H-bridging, but to the differences in steric energy between the alkenes and cation. As the chain becomes smaller, the van der Waals interactions between the *in*-hydrogen and the double bond become stronger, and they can be relieved by formation of the carbocation. The μ -H-bridging plays then a minor role. For **89B**, the pK_a is estimated from the experimental data to be near -1, while that for **89C** is expected to fall between -3 and -8. By using the calculated heats of formation for cations and alkenes (assuming that $\Delta\Delta H \approx \Delta\Delta G$ and that the $pK_a = -1$ for **89B**), the calculated pK_a 's for the series **89E-A** become -6.0, -5.3, -1, and +10. The calculated value for **89C** falls inside the range expected from the experimental data. Furthermore, **89A** is expected to be an extremely weak acid, being able to exist even in water. Its synthesis will allow the confirmation of this prediction.

10. Crystal Structures for Carbocations

The first crystal structure of an aliphatic carbocation, the $Sb_2F_{11}^-$ salt of the 3,5,7-trimethyl-1-adamantyl carbocation (**92**), was reported by Laube in 1986.¹⁰³ The adamantyl cage clearly shows hyperconjugation effects on bond lengths and bond angles. The cationic center is almost planar. The C-C bonds β to the cationic center are longer than the average (1.62 Å). This, along with the small C₁-C₂-C₃ angle (99°) suggest that C₂, C₈, and C₉ have near sp² hybridization. The p-like orbital is then involved in hyperconjugation with the cationic center (Scheme XIV).

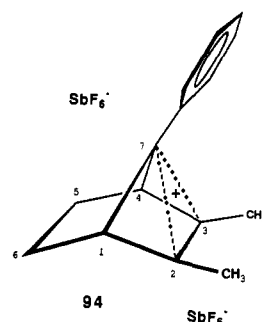
More recently, the first crystal structure of a norbornyl cation was reported for the $Sb_2F_{11}^-$ salt of the *anti*-1,2,4,7-tetramethyl-2-norbornyl cation (**93**), which is formally a tertiary ion.¹⁰⁴ The ion was found to have no symmetry.



The structure exhibits a weakened C₁-C₈ bond (1.742 Å) and a shortened C₁-C₂ bond (1.44 Å), evidencing electron donation to the cationic center. The C₂-C₁-C₆ angle and the C₂-C₆ distance (81.6°, 2.09 Å) clearly indicate unsymmetrical σ -bridging. C₂ is almost planar, while C₁ displays slight pyramidalization, evidence of a larger partial charge at C₂. Two units of $Sb_2F_{11}^-$ are present in the crystal. It is interesting to compare these striking results with the results of isotopic perturbation of 1,2-dimethyl norbornyl cation,¹⁰⁵ where an isotope-induced splitting of the C₁ and C₂ is seen, but with a value much smaller than that observed for the 1,2-dimethylcyclopentyl cation. This was interpreted as indicating a partially bridged unsymmetrical structure.

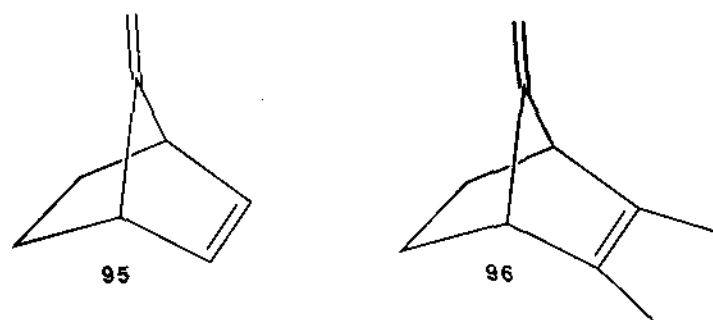
Overall, the structure is much more similar to the calculated geometry of the symmetrical 2-norbornyl cation than to that of norbornane. This was not expected, because of the tertiary nature of the ion. It is concluded that the skeleton of 2-norbornyl cations generally favors bridging.

Attempting to assess the nonclassical character of 7-norbornenyl cations, Laube isolated the SbF_6^- salt of the 2,3-dimethyl-7-phenyl-2-norbornen-7-yl cation (**94**).¹⁰⁶ The crystal structure shows the carbon skeleton



surrounded by two SbF_6^- , with no overall symmetry. Nevertheless, the cation has a plane of symmetry within the skeleton. Worth mentioning is the short distance between the cationic carbon (C₇) and both C₂ and C₃ (1.86 Å), which makes the C₇ and C₂-C₃ bridges approach to one another, strongly deforming the structure (the dihedral angle C₃-C₄-C₁-C₇ = 91.7°). Remarkable also is the fact that the C₂-CH₃ and C₃-CH₃ bonds are slightly bent toward C₇, while the bond connecting the phenyl ring is slightly bent toward the C₂-C₃ bridge. The C₂-C₃ bond distance is 1.38 Å, longer than a normal double bond. The anions are found to be close to the carbons bearing the positive charge, particularly C₇ and C₂.

Molecular mechanics calculations on the model systems 7-methylene-2-norbornene (**95**) and 2,3-dimethyl-7-methylene-2-norbornene (**96**) and ab initio calculations on the 2-norbornene-7-yl cation (**10**) allowed the evaluation of the π -resonance energy. It was estimated that the energy necessary to overcome the



torsional strain and produce the bending of the bridges, corresponds to 0.75 of that calculated for **10**. HMO theory predicts resonance energies between -15 and -35 kcal/mol for **94**. This value can be compared with the resonance energies calculated by the same method for **10**, -25 to -50 kcal/mol, suggesting that despite the fact of the phenyl ring, the ion stabilizes itself by formation of an aromatic three-center two-electron system.

The possibility that the observed structure was the average of two rapidly equilibrating classical ions was also considered. Nevertheless, careful analysis of the probability density functions, and their comparison of what would be expected for the ions in equilibrium ruled out this possibility. A similar evaluation was done to **93**,¹⁰⁴ but no evidence of hidden disorder was found either.

Laube also analyzed another interesting aspect of the crystal packing. The position of the anions surrounding **94** suggests easy attack of nucleophiles from the same direction. It is then expected, for this cation, that products of 7-anti and 2-endo attack be formed in comparable amounts. The fact that 2-endo attack is not observed experimentally is explained on the grounds of the thermodynamic stability of both products, that is, equilibration under acidic conditions to give the more stable product, that originating from 7-anti attack. A similar correlation is found for **76**, in which the SbF_{11}^- units seem to attack C_2 from the exo and endo sides. However steric and stereoelectronic effects (the location of the anions) seem to favor the product of 2-exo attack over that of 2-endo attack, in agreement with experimental results. Two more cases are analyzed, and a clear correlation is found between crystal packing and the solvolysis behavior of carbocations.

11. New Methods of Investigation of Carbocations¹⁰⁷

Vančik and Sunko developed a new method for obtaining IR spectra of carbocations in the solid state.¹⁰⁸ By using a nitrogen-cooled cryostat, the precursor and SbF_5 are deposited in vacuo on a liquid nitrogen-cooled CsI window at a ratio of 1:5. The resulting matrix is then warmed to 150 K, and the spectrum taken. Using this technique, the authors were able to obtain the IR spectrum of the 1-methylcyclopentyl cation (**59**), using 1-chloro-1-methylcyclopentane as precursor.

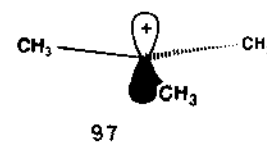
At 150 K, the IR spectrum of the ion was completely different from that observed in the neutral precursor, specially the region of C-H stretching and bending. The intense absorption at 2775 cm^{-1} is assigned to the stretching of C-H bonds adjacent to the cationic center. The 220-cm^{-1} shift to lower frequency is ascribed to hyperconjugation, which weakens this C-H bond. A shift to lower frequencies is also observed for the C-H deformation bands. The strongest peak appears at 1280

cm^{-1} and is assigned to the stretching of the carbon bonds of the cationic center. When cyclohexyl chloride was used as precursor, the same IR spectrum is obtained, showing that rearrangement occurs even in the solid state below 150 K. The assumption that the shift to lower frequencies of the stretching of the C-H bonds adjacent to the cationic center is due to hyperconjugation is further supported by high level ab initio calculations (MP2-FULL/6-31G**) on the unsubstituted cyclopentyl cation.¹⁰⁹

Recently, Koch carried out high-level ab initio calculations (MP2/6-31G*), which confirm that the non-classical structure of the 2-norbornyl cation (**1**) with C_8 symmetry is an energy minimum in the gas phase.¹¹⁰ Vibrational analysis at the same level of theory showed only positive frequencies. In an additional paper,¹¹¹ the set of calculated frequencies was compared with the experimental IR spectra of the 2-norbornyl cation, obtained by the method of Sunko and Vančik.¹⁰⁸ Because of the known tendency of the MP2/6-31G* calculations to overestimate the vibrational frequencies, a scaling factor was applied to the theoretical frequencies. The agreement between calculated and experimental spectra is good if one assumes that the assignment of the lines is correct. These results further support that the 2-norbornyl cation in SbF_5 has a bridged structure.

Detailed structural information about reactive carbocations is not very easy to obtain by diffraction methods. Only very few carbonium ion salts can produce crystals good enough to be used for X-ray crystallography. On the other hand, nutation NMR spectroscopy is a method that can potentially measure internuclear distances to $\sim 1\%$ accuracy in solids, without requiring high crystalline order.¹¹²

Yannoni and co-workers used this method to obtain the geometry of the *tert*-butyl cation (**97**).¹¹³ Because it determines the distance between two magnetic nuclei, two ^{13}C -dilabeled solid ions were prepared from the corresponding chlorides in SbF_5 . One isomer was used

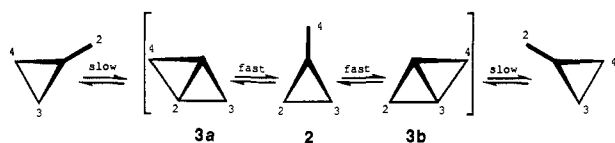


to measure the distance between the cationic carbon and the methyls, and the other allowed for the determination of the distance between two methyls. The NMR spectra of both solids were obtained and compared with calculated spectra. The best fit for the C^+-CH_3 distance was found to be between 1.46 and 1.47 Å, while it was 2.51 Å for the CH_3-CH_3 distance. This results are in close agreement with high-level ab initio calculations (MP2/6-31G*).¹¹⁴ From this data, the C-C-C angle turns out to be 120° .

Low-temperature NMR of carbocations in the solid state has been used for some time;^{31,38,115} however, it has not become a general method. The recent construction of an NMR probe for CPMAS experiments at temperatures near that of liquid helium¹¹⁶ has allowed the observation of two of the most studied yet still controversial carbocations.

As a continuation of previous low-temperature spinning (at 77 K) and nonspinning (at 5 K) NMR spectra of the 2-norbornyl cation (**1**),³⁸ Myhre, Webb, and Yannoni obtained its CPMAS ^{13}C NMR spectrum down to 6 K.¹¹⁷ It was observed that the band at 125 ppm

SCHEME XV

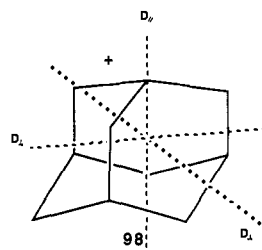


and which was previously assigned to C_1 and C_2 remains unchanged in the range 120–6 K. This further supports the absence of both, a dynamic process between two equilibrating classical 2-norbornyl cations and heavy-atom tunneling. What the NMR data clearly implies is the absence of a significant barrier, and hence the presence of a single minimum in the potential energy surface of the ion.

Myhre, Webb, and Yannoni also obtained the CPMAS ^{13}C NMR of the C_4H_7^+ cation (^{13}C -labeled at the methylene carbons) between 170–5 K.¹¹⁸ As previously mentioned, experimental studies and theoretical calculations suggest the presence of two energy minima for this system, a bicyclobutonium ion (3) and a cyclopropylcarbinyl cation (2) in rapid equilibrium over a rather flat energy surface.^{14–16} Below 60 K, four bands are observed at 235, 55, 28, and –15 ppm. At 60 K, two additional bands at 104 and 40 ppm are noticed. As the temperature drops, the band at 235 ppm decreases in intensity while that at –15 ppm gets larger. From these bands, the ΔH for the equilibrium process is estimated to be near 0.05 kcal/mol under the experimental conditions, favoring 3. It is also observed that the band at 28 ppm moves slightly to higher field, being its chemical shift 23 ppm at 15 K. From comparison of this data with the chemical shifts calculated with the IGLO method on both intermediates,^{11,16} the band at 235 ppm is assigned to the cationic methylene of 2 and that at –15 ppm to the hypercoordinated carbon in 3.

The behavior of the band at 28–23 ppm, which is by itself evidence of an equilibrium, is ascribed by the authors to averaged methylenes (C_2 – C_3 , Scheme XV) under conditions of constrained exchange. In other words, the presence of the ion in glassy SbF_5 matrix does not allow for all possible rearrangement processes to occur, but only a subset of them. The observed spectra can be explained by assuming that only the interconversions shown in Scheme XV take place and that the contribution of the cyclopropylcarbinyl cation is minimum at the lower temperatures, increasing as the temperature rises. The fact that the line assigned to the average of C_2 – C_3 is observed even at 5 K suggests that the activation energy necessary to go from 3 to 2 is very small, in the order of a few tenths of a kilocalorie. In conclusion, the experimental data agrees very well with theoretical calculations.

Even though stable solutions of carbocations in superacids have been with us for a relatively long time, the interaction of the species present in solution is not well understood. Kelly and Leslie addressed this issue from an interesting point of view,¹¹⁹ the main idea being that the interaction between a carbocation with a counterion and/or solvent should be reflected in the anisotropy of its rotational orientation. In other words, for an associated molecule, tumbling would be expected to be slower through the axis involving greater movement of the complexed cationic center. By using this model, the interactions between the 1-adamantyl cation (98) and medium were studied.



^{13}C spin-lattice relaxation times and NOE's for the three different types of carbons attached to protons were determined for each set of experimental conditions. From this data the dipole–dipole relaxation times (T_{1}^{DD}) were calculated, and from them the rotational information was obtained by using Woessner's equations.¹²⁰ Assuming that the cation acts as an axially symmetric ellipsoid, the diffusion coefficient for rotational reorientation about the two equivalent minor axes (D_{\perp}) and the anisotropy (σ) were obtained (σ is the ratio between the diffusion coefficient of rotation between the C_{3v} axis of symmetry (D_{\parallel}) and the minor axis). The rotational anisotropy was determined as a function of temperature, superacid, precursor, solvent, and concentration. It was found that σ varies depending on the experimental conditions, evidencing different types of cation–medium interaction.

The 2-adamantyl cation was generated from the corresponding alcohol or chloride. The almost constant values of σ indicate that the interactions of the adamantyl cation with counterions is practically independent of the precursor. It was also observed that the alcohol did not ionize until warmed at –30 °C. On the other hand, σ was found to be solvent dependent. When SO_2 was used, $\sigma \approx 1$, while in SO_2ClF σ was always greater than 1. This is interpreted as larger interaction of the cation with the solvent, and hence greater stabilization in SO_2ClF than in SO_2 . It was also observed that the degree of interaction diminishes as the concentration of acid increases. In addition, the overall small values of σ suggest that the adamantyl cation does not reorient as an ion pair, and the observed anisotropy is the result of interaction between the cationic center and a diffuse cloud of negative charge. The authors finally suggest that "...any carbocations with less charge localization at the cationic center than adamantyl will also not reorient as part of a long-lived ion pair."

12. References

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