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Deuterium Isotope Effects on the Carbon-13 Chemical Shifts in 2-Substituted-2-Norbornyl Cations*

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Deuterium isotope effects on carbon-13 chemical shifts have been determined for 2-methyl-2-norbornyl-2-d_1 cation, 2-methyl-2-norbornyl-*exo*-6-d_1 cation, 2-methyl-2-norbornyl-*endo*-6-d_1 cation, 2-methyl-2-norbornyl-*exo,exo*-5,6-d_2 cation, 2-methyl-2-norbornyl-*exo, anti*-6,7-d_2 cation, 2-aryl-2-norbornyl-1-d_1 cation, 2-aryl-2-norbornyl-*exo*-6-d_1 cation, 2-aryl-2-norbornyl-*endo*-6-d_1 cation, 2-aryl-2-norbornyl-*exo,exo*-5,6-d_2 cation, and 2-aryl-2-norbornyl-*exo,anti*-6,7-d_2 cation. The deuterium isotope effects exhibit different magnitudes for the different isotopomers. For the 2-methyl-2-norbornyl cation, the isotope effect at C_2 is 1.4 ppm for *exo*-6-d_1, 0.9 ppm for *endo*-6-d_1, and 0.1 ppm for 1-d_1. Large positive 3-bond isotope effects are highly unusual but are consistent with the bridged structure for this ion. The isotope effects, ΔC(D), at the cation center have been plotted *vs.* σ^{c+} constants for each of the deuterated 2-aryl-2-norbornyl cation series and compared to plots of the isotope effects, ΔC(D), *vs.* ^{13}C chemical shifts at the cation center. The nonlinear behavior of these plots is consistent with the onset of bridging. The onset of delocalization in the 2-aryl-2-norbornyl cation as a result of electron withdrawing groups on the phenyl ring gives enhanced positive values for the isotope shifts at C_2 for deuterium substitution at C_6 and reduced positive values for deuterium substitution at C_1. Isotopic substitution appears to readily perturb the vibrational averaging occurring in the relatively flat anharmonic potential well for these systems as the electron demand increases.

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* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.
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INTRODUCTION

A number of studies over the past thirty years have tried to clearly establish evidence for the existence of nonclassical cations.[1] Since the development of carbon-13 NMR spectroscopy, an analysis of the carbon-13 NMR chemical shifts of the norbornyl-type cations appears to have convincingly demonstrated their nonclassical nature under long-lived, stable ion conditions.[2] There are a number of reports[3] dealing with norbornyl-type carbocations. The methods developed by Olah to generate and observe stable carbocations in superacid solutions were successfully applied to direct observations of the norbornyl cation.[4] The larger upfield chemical shift of the C_1, C_2, and C_6 carbons compared to carbons at cationic centers in other ions clearly supports the bridge structure for the norbornyl cation.

Yannoni and co-workers[5] have studied the norbornyl cation by solid state ^{13}C NMR spectroscopy using cross polarization magic angle spinning techniques at a remarkable low temperature (5 K). At such low temperatures, it should be possible to distinguish readily between a rapidly equilibrating pair of classical cations and a static, symmetrically bridged species. They reported that the hypothetical 1,2-Wagner-Meewein shift could be occurring but with a barrier less than 0.2 kcal/mol. This result further supports the σ-bridged nature of the 2-norbornyl cation.

The deuterium isotopic perturbation technique has been developed over the past several years. By observing the changes in ^{13}C NMR spectra produced by deuterium isotopic perturbation equilibrating ions can be distinguished from bridged systems. Sorensen and Ranganayakulu reported[7] the equilibrium isotope effects of the 2-norbornyl-$h_{10}d_1$ cation. The largest equilibrium isotope effects are observed between the H-5 and H-7 protons. Their results agree with the conclusion that the 2-norbornyl cation is either a symmetrical cation or a pair of nearly symmetrical cations separated by an extremely small barrier.

Isotopic substitution by deuterium also affects the carbon-13 chemical shifts in static systems. The majority of deuterium induced isotope shifts of carbon-13 chemical shifts are to higher field and decrease rapidly with distance. The one-bond isotope shifts could be readily explained by the vibrational origin of isotope effects. Long range isotope effects, although of vibrational origin, are more difficult to rationalize. They can be best understood as indicating a change in electron distribution resulting from an isotopic perturbation of the vibrational average over an anharmonic potential well. Recently some interesting and unusual upfield and downfield long range deuterium isotope shifts have been reported.[8] These shifts have been discussed in terms of isotopic perturbation of resonance, perturbation of hyperconjugation, through space perturbation of resonance, angular dependence and steric effects.[9] Extensive studies of the deuterium isotope effect on the ^{13}C chemical shifts of 2-substituted-2-norbornyl cations by Servis, *et al.*[10] have led to a further understanding of the relationship between the isotope shift and charge delocalization of the carbocations.

The mechanism for the rearrangement of the 2-methyl-1-norbornyl cation from its *exo*-3-*d* isotopomer to the *endo*-3-*d* isotopomer has also been reported.[11] As a result of this rearrangement, the following proton and carbon nuclei are interchanged.

H-3 (*exo*) ↔ H-3 (*endo*)
H-5 (*exo*) ↔ H-7 (*anti*)
C-5 ↔ C-7
H-5 (*endo*) ↔ H-7 (*syn*)
H-6 (*endo*) ↔ H-1
C-1 ↔ C-6

Since the deuterated carbon shows a triplet signal in the ^{13}C NMR spectrum, it is relatively easy to observe the nuclear interchange by NMR. In order to complete the study, the rearrangement of 2-substituted-2-norbornyl cations with deuterium substitution at *exo*-C_5 or *endo*-C_6 positions would provide useful evidence to support the mechanism of the rearrangement.

The nature of electronic effects in cationic reactions has been studied by application of the Gassman-Fentiman tool of increasing electron demand.[12] Brown has introduced σ^{c+} constants[13] with which to correlate the cationic carbon chemical shifts of aryl-substituted carbocations; σ^{c+} values ranged from –2.02 for the most electron-donating *p*-methoxy substituent to 1.03 for the most electron withdrawing 3,5-bis(trifluoromethyl) substituent.[14]

Olah and coworkers reported that the carbon-13 chemical shifts of the cationic carbons of a series of carbocations have an approximately linear relationship between these chemical shifts and Brown's σ^{c+} constants.[13] Using the tool of increasing electron demand, plots of 2-aryl-2-norbornylcation $C_2{}^+$ chemical shifts *vs.* σ^{c+} demonstrate the onset of σ-bridging in this system. Servis has also reported that graphs of isotope shifts at the cationic center, $^2\Delta C_{2+}$, *vs.* σ^{c+} for the deuterated 2-aryl-2-norbornyl cations indicated the onset of σ-delocalization.[10] They concluded that the observed $^2\Delta C(D)$ isotope shift at the cationic center was a sum of contributions from a small upfield isotope shift due to perturbation of the σ-framework, a downfield shift due to perturbation of hyperconjugation, and a large upfield shift from perturbation of two electron, three-center bonding. The nonlinearity of the plots are best explained as indicating the onset of σ-bridging with increasing electron demand.

We now wish to report deuterium-isotope effects on the carbon-13 chemical shifts of the 2-methyl-2-norbornyl cation and the 2-aryl-2-norbornyl cations resulting from deuterium substitution at the *exo*-6-d_1, *endo*-6-d_1, 1-*d*, *exo,exo*-5,6-d_2, and the *exo,anti*-6,7-d_2 positions.

RESULTS AND DISCUSSION

Deuterated isotopomers of 2-norbornanone were used to prepare the 2-substituted-2-norbornanols which were used as immediate precursors to the 2-substituted-2-norbornyl cations. The NMR parameters of 2-norbornanone have been thoroughly studied.[15] Some of the earlier difficulties[16] in the analysis of norbornyl derivatives were resolved by Marshall using unsymmetrically deuterated systems.[15]

We have used a ring opening reaction of nortricyclene with deuterioacetic acid to prepare 6-deuterated norbornyl derivatives.

Monodeuterated Isomers

Nortricyclene was prepared by reaction of norbornene with *N*-bromosuccinimide followed by conversion of bromonortricyclene to its Grignard reagent and subsequent hydrolysis.[17] The process of deuteration has been observed for the reaction in D_2SO_4–DOAc, and the ring opening of nortricyclene produces a mixture of 2-*exo*-norbornyl-*endo*-6-d_1 acetate and 2-*exo*-norbornyl-*exo*-6-d_1 acetate.

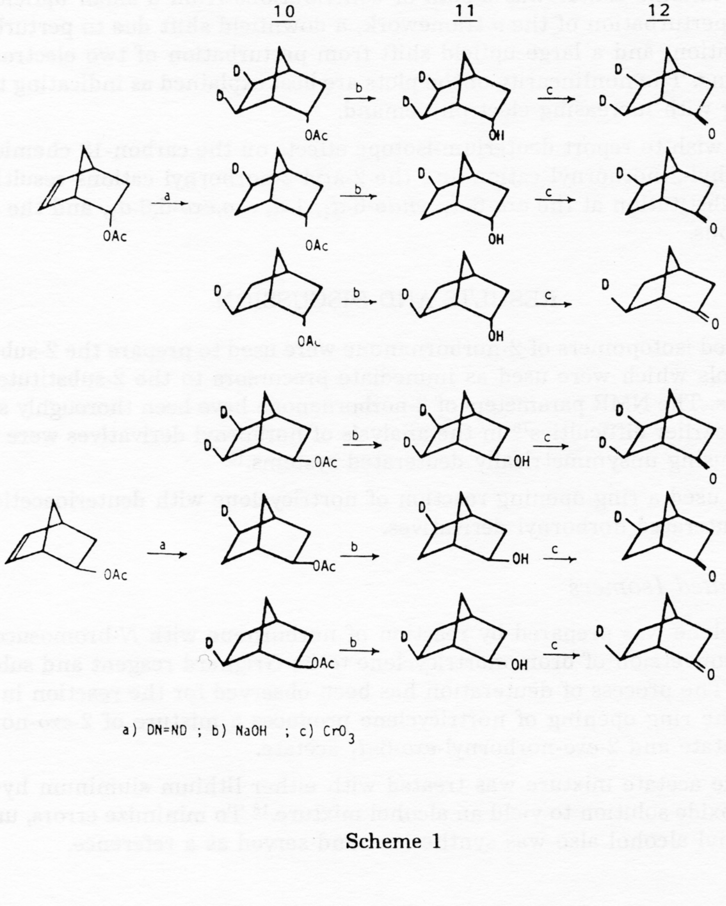
The crude acetate mixture was treated with either lithium aluminum hydride or sodium hydroxide solution to yield an alcohol mixture.[18] To minimize errors, unlabeled *exo*-2-norbornyl alcohol also was synthesized and served as a reference.

The oxidation of hydroxy groups to ketones has been in general accomplished by use of chromic acid. Oxidation of the deuterated alcohols to the corresponding deuterated ketone was accomplished with chromium trioxide in pyridine under general conditions known not to induce skeletal change.[19] In considering the stereochemistry of the ketones, it is clear that the deuterium at carbon-6 remained at its original position.

Dideuterated Isomers

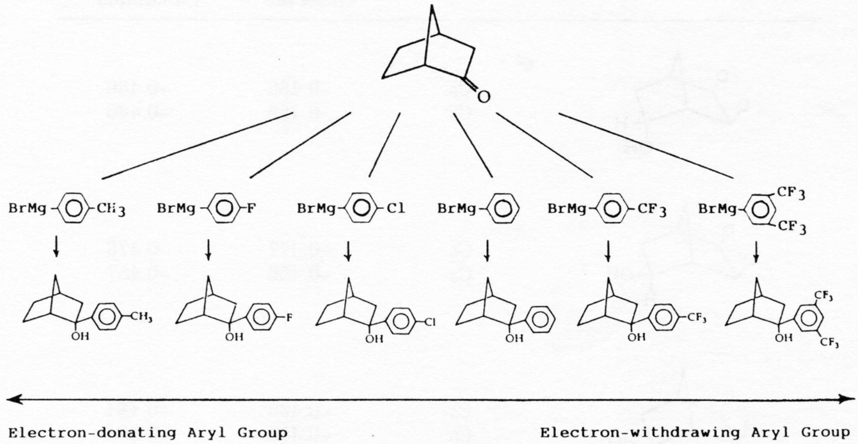
The *exo,exo*-5,6-dideuterionorcamphor in which we were interested was prepared as reported by Marshall.[15] Since the original 5-norbornenyl acetate (from Aldrich) was an *exo,endo*-mixture, the deuterated product was synthesized and also appeared as an *exo,endo*-mixture. Thus, the various deuterated products in Scheme 1 are of real interest and their products also have been examined by ^{13}C NMR spectrum. The acetate product mixture was hydrolyzed to give a crude alcohol as a semisolid. The alcohol was oxidized by Sarett oxidation to form the corresponding deuterated norcamphor.

In order to apply σ^{c+} correlations to the study of neighboring group participation in carbocations, we needed to synthesize a wide variety of 2-aryl-2-norbornyl alcohols.



Scheme 1

The most common way to the desirable aryl substituted 2-norbornyl alcohols was the addition of organometallic reagent to 2-norbornanone. The various Grignard reagents reacted at the carbonyl group of 2-norbornanone to give the magnesium derivatives of alcohols which are converted into alcohols by treatment with dilute acid, Scheme 2.



Scheme 2

The chemical shift isotope effects were determined by comparison of the ^{13}C chemical shifts of those alcohols with their corresponding deuterated isotopomers. In all the alcohols, the largest isotope shifts were at the directly deuterated α-carbon positions. All isotope shifts are to higher field.

The additivity of isotope effects has also been discussed. For several compounds, the isotope effects in the individual monodeuterated and dideuterated isotopomers were determined. These results can be used to demonstrate the additivity of isotope effects in these alcohols (Table I). The deuterium isotope effects for the dideuterated isotopomers are the sum of deuterium isotope shifts of two individual monodeuterated isotopomers. For instance, the deuterium isotope effects for *exo,exo*-5,6-d_2 alcohols are equal to the deuterium isotope effects of *exo*-5-d_1 alcohol plus *exo*-6-d_1 alcohols.

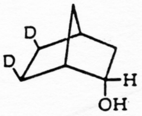
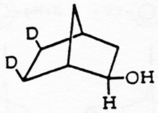
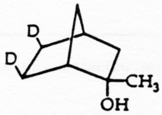
Carbocations

Antimonypentafluoride, SbF_5, is very good Lewis superacid together with SO_2ClF. The fact that it has a low freezing point and it is not too viscous makes it a very useful superacid for low temperature studies and in particular for NMR spectroscopy.[20]

When a tertiary-2-substituted-2-norbornyl alcohol is dissolved in SbF_5/SO_2ClF at –78 °C a stable and light yellow colored solution of the corresponding tertiary carbocation is formed. 2-Methyl, 2-phenyl and other substituted 2-phenyl-2-norbornyl alcohols give the corresponding carbocations in SO_2ClF at low temperature. Depending upon the nature of the 2-substituent group, these ions can give a relatively wide range (1.5 ppm) of deuterium isotope effects for $^{2}\Delta C_{2+}(3,3\text{-}d_2)$.

TABLE I

Additivity of Isotope Effects on the Carbon-13 Chemical Shifts.

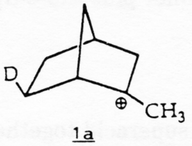
Compound	Carbon	Isotope Effect, ppm	
		Observed(a)	Calculated(b)
	C_5	−0.486	−0.486
	C_6	−0.485	−0.486
	C_5	−0.477	−0.478
	C_6	−0.456	−0.457
	C_5	−0.485	−0.484
	C_6	−0.485	−0.484

(a) Measured directly from *exo,exo*-5,6-d_2 isotopomers

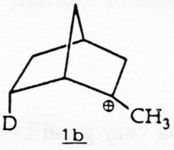
(b). Calculated by adding data from *exo*-5-*d* and *exo*-6-*d* together

2-Methyl-2-norbornyl Cation. 1

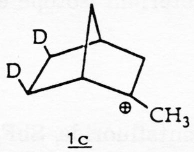
Large upfield isotope shifts at the cation center in the 2-methyl-2-norbornyl cation have been reported. The sum of the isotope shifts for *exo*-3-d_1 and *endo*-3-d_1 of the 2-methyl-2-norbornyl cation adds up to the isotope shift for C_2 in the 3,3-d_2 isotopomer. The 2-methyl-d_3-2-norbornyl cation exhibits an isotope shift at C_2 of 2.2 ppm upfield. This large upfield effect has been attributed to an isotopic perturbation of resonance instead of an equilibrium isotope effect. Most notable for these previously reported labeled ions are large upfield shifts, $^2\Delta C(D)$, at the cation center C_2.



1a



1b

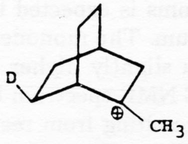


1c

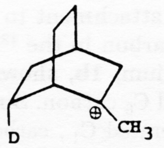
On the other hand, the 2-methyl-2-bicyclo[2.2.2]octyl-6-d_1 cation, **2**, shows a smaller downfield isotope shift (0.44 to 0.55 ppm). For these ions, it was difficult to make assignments between *exo*-6-d_1, **2a** and *endo*-6-d_1, **2b**.

Thus, examination of deuterium isotope shifts of the 2-methyl-2-norbornyl cations with deuterium at C_6 position should be very interesting.

Carbocations and their corresponding unlabeled compound, were prepared by dropwise addition of a solution of the precursor alcohols in SO_2ClF to a vortex-stirred



2 a

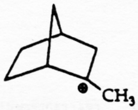


2 b

solution of SbF_5 in SO_2ClF at –150 °C (pentane – liquid N_2 bath). It was very important to prepare all the deuterated 2-methyl-2-norbornyl cations at such low temperatures to avoid scrambling of the label. The samples then were frozen in liquid nitrogen until the NMR tube was inserted into the NMR probe at –110 °C. The ^{13}C NMR spectrum of the cationic centers are shown in Figures 1 (a) and (b). It is clear that large downfield isotope shifts are observed at C_2 without any deuterium scrambling problems. If the cation solution was allowed to warm up to about –80 °C or the cation solution was prepared at –100 °C (dry ether-acetone bath), rapid scrambling occurred as can be seen in Figure 1 (c) and (d). Although it was not possible to make assignments of all the isotope shifts at C_2, it was possible to assign isotope shifts to those major isotopomers in which we are interested. The results are summarized in Table II.

TABLE II

Deuterium Isotope Effects on the Carbon-13 Chemical Shifts of 2-Methyl-2-norbornyl Cation.(a)

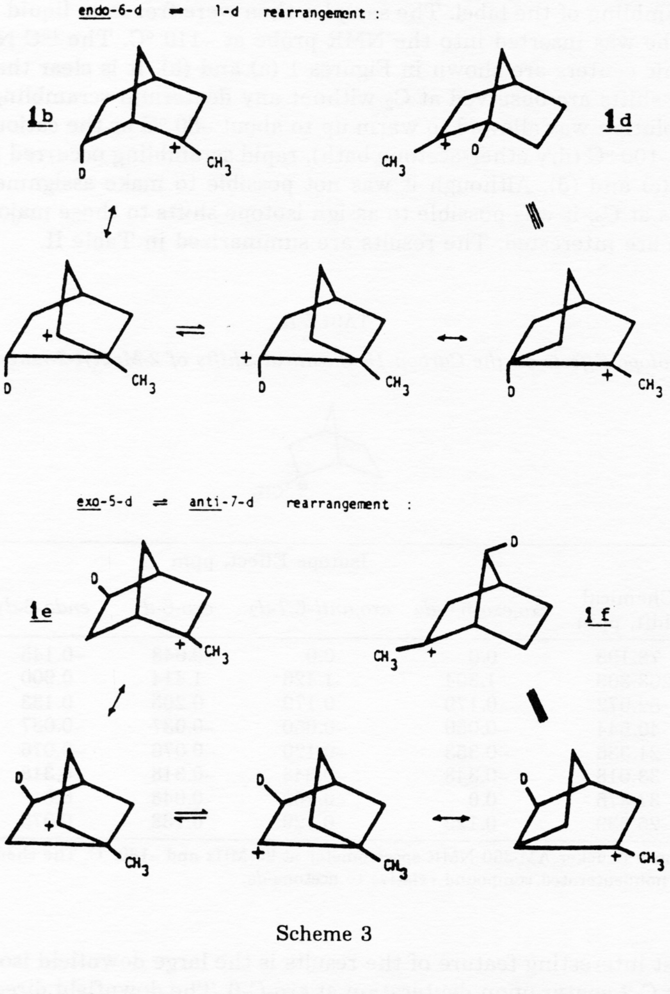


Carbon	Chemical shift, ppm	Isotope Effect, ppm				
		exo,exo-5,6-d_2	*exo,anti*-6,7-d_2	*exo*-6-d_1	*endo*-6-d_1	1-d_1
C1	78.193	0.0	0.0	–0.048	–0.145	–0.145
C2	268.309	1.304	1.426	1.414	0.900	0.112
C3	52.972	0.179	0.179	0.205	0.133	0.0
C4	40.544	–0.050	–0.050	–0.037	–0.037	0.0
C5	21.335	–0.353	–0.120	–0.076	–0.076	0.0
C6	33.018	–0.348	–0.348	–0.318	–0.318	–0.126
C7	37.875	0.0	–0.250	0.048	0.0	–0.157
C8	25.839	0.129	0.129	0.138	0.075	0.0

(a) Acquired on a Brucker AM-360 NMR spectrometer at 90 MHz and –130 °C. The chemical shift given is that of the nondeuterated compound relative to acetone-d_6.

The most interesting feature of the results is the large downfield isotope shift (1.4 ppm) for the C-2 center upon deuteration at *exo*-C-6. The downfield direction indicates that in the deuterated isotopomers, the positive charge density at the cation center is greater. The relatively larger deuterium isotope shift for the C_6, C_7-*exo,anti*-dideuterated cation (1.4 ppm) than for the C_6-*exo*-monodeuterated cation results from the additivity of the isotope effects.

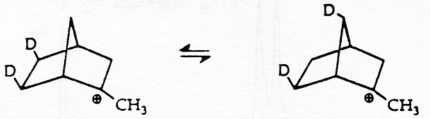
Deuterium atom attachment to the carbon atoms is expected to give a triplet for the directly bonded carbon in the ^{13}C NMR spectrum. The monodeuterated C_6 carbon with the *endo*-deuterium, **1b**, shows a triplet at a slightly higher field than the corresponding unlabelled C_6 carbon. Similarly, the ^{13}C NMR spectrum is expected to show a triplet for the deuterated C_1, carbon in the ion resulting from rearrangements of the *endo*-d_6 deuterated ion. Thus, these ions are rapidly equilibrating through a hydride shift. Rearrangement of the ion resulting from ionization of the precursor alcohol deuterated at *exo*-C_5 also leads to a non-equivalent pair of isotopomeric ions (Scheme 3).



Scheme 3

Again, this pair of ions is rapidly produced through a 1,6-hydride shift so that the spectrum of this mixture of monodeuterated cations also exhibits triplets for the *exo*-C_5 and *anti*-C_7 positions. Unfortunately, we were unable to prepare the pure *exo*-5-d_1, isotopomer, **1e**. It was possible to prepare it as a minor isotopomer in a mixture together with a dideuterated *exo,exo*-5,6-d_2 isotopomer, **1c**. Ionization of *exo,exo*-5,6-

d_2-2-methyl-2-norbornanol generates another interesting pair of dideuterated cations **1c** and **1g**. The ^{13}C NMR spectrum of this pair of cations displays two peaks for the cationic carbon C_2, Figure 1 (b). The ^{13}C NMR spectrum is consistent with two different species at equilibrium. The carbon-13 chemical shift differences relative to the unlabelled cation gives the deuterium isotope effects which are the differences we have measured (1.4 ppm). In addition to the *exo,exo*-5,6-d_2-2-methyl-2-norbornyl cation, **1c**, a new and considerable quantity of a rearranged isomer is produced which has dideuterium substitution at both the *exo*-C_6 and *anti*-C_7 positions, **1g**. In fact, in our experiment, an almost equal distribution of this rapidly equilibrating pair of cations was realized judging from the intensity of the carbon peaks.



1c 1g

When the cation solution was warmed to –80 °C, the cation pair rearranged to give other deuterated isotopomeric cations. The rearrangement caused the intensity of the C_2 peaks, **1c** and **1g** to decrease and other C_2 peaks to appear.

The downfield isotope shift of all these cations are quite interesting. Labeling at the C_6 position involves isotopic substitution three bonds away from the cationic center and still causes large deshielding effects at C_2. These three bond isotope effects from C_6 deuterium substitution can not be due to hyperconjugation. Instead, isotopic perturbation of resonance is likely to be the major factor. This perturbation results from averaging over a vibrational potential energy distribution and changes the averaged electron distribution for different isotopomers.

The α-deuterated chemical shift isotope effects in these carbocations are relatively easy to understand. Most of the values of α-isotopic splittings are –0.3 ppm for one bond deuterium isotope effects for C_5, C_6 and C_7. At the C_1 position, a small value (–0.14 ppm) was observed. This result is not understood but may be a result of a different carbon hybridization at this position. The additivity principle was applied to the dideuterated *exo,exo*-5,6-cation to give the calculated deuterium isotope effects for individual monodeuterated isotopomers. For example, the deuterium isotope shifts at caionic carbon, C_2, was 1.41 ppm for the *exo*-6-d_1 cation, 1.30 ppm for the *exo,exo*-5,6-d_2 cation and 1.43 ppm for *exo,anti*-6,7-d_2 cation. As a result, the C_2 carbon of the *exo*-5-d_1 cation is predicted to have a –0.1 ppm isotope shift and the C_2 carbon of the *anti*-7-d_1 cation a –0.02 ppm isotope shift.

The isotope scrambling from the *endo*-6-d_1 to the 1-d_1 position provides very good evidence to support the view that the deuterium at carbon-6 rapidly rearranges to carbon-1. For this pair of *endo*-6-d_1 and 1-d_1 cations, the larger isotope effect for the cationic carbon-2 results from deuterium at the *endo*-6 position. The bigger isotope perturbation effect of the *exo*-C_6 is the source of the *exo/endo* difference for isotope shifts. Figure 1 shows the comparison of the 267.5 to 272.5 ppm region in the ^{13}C NMR spectrum of various 2-methyl-2-norbornyl cations.

The proposed mechanism for the interconversion of the 2-methyl-2-norbornyl-*exo,exo*-5,6-d_2 and the 2-methyl-2-norbornyl-*exo,anti*-6,7-d_2 cations, **1a**, can also be

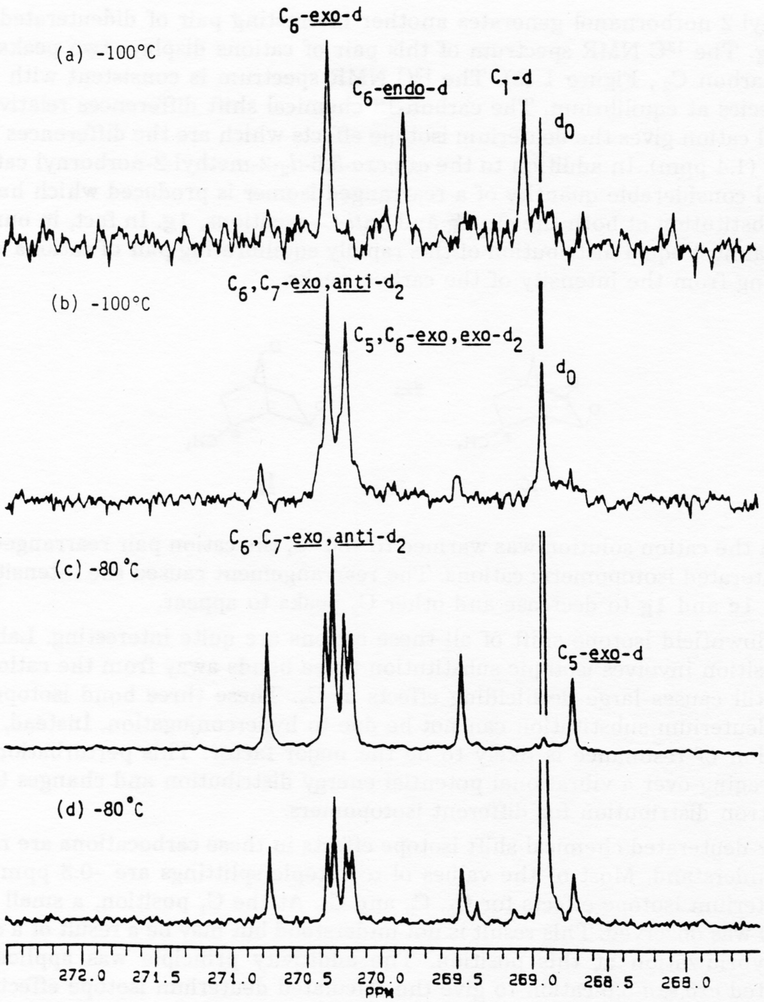


Figure 1. ^{13}C NMR chemical shifts of the cationic center C_2 of the 2-methyl-2-norbornyl cations. (a) from 2-methyl-2-norbornanol-6-d_1 prepared at −135 °C, spectral acquisition at −100 °C; (b) from 2-methyl-2-norbornanol-*exo,exo*-5,6-d_2 with added 2-methyl-2-norbornanol-d_0, prepared at −135 °C, spectral acquisition at −100 °C; (c) from 2-methyl-2-norbornanol-*exo,exo*-5,6-d_2 prepared at −100 °C, spectral acquisition at −80 °C; (d) from 2-methyl-2-norbornanol-*exo,exo*-5,6-d_2 with added 2-methyl-2-norbornanol-d_0, prepared at −100 °C, spectral acquisition at −80 °C.

studied by two-dimensional heteronuclear correlation NMR spectroscopy. The method of two-dimensional proton/carbon chemical shift correlation spectroscopy of these cations was used to establish the assignment of the proton spectrum by relating it to the previously assigned carbon spectrum. This technique has been applied in various forms to provide information on the connectivity of molecular carbon frameworks.[21] Here, the deuterium positions are easy to assign. A knowledge of the assignment of the carbon spectrum can be used to provide assignments in the proton spectrum which may give the information about the cation rearrangements.

Figure 2 shows the proton-carbon correlation spectrum of the cationic mixture which results from rearrangement following ionization of 2-methyl-2-norbornanol-*exo,exo*-5,6-d_2. This experiment shows two types of cations: the *exo,exo*-5,6-d_2 cation, **1c**, which comes directly from the original precursor and the *exo,anti*-5,7-d_2 cation, **1g**, which results from rearrangement. Since the carbon spectrum of 2-methyl-2-norbornyl cation has been assigned, the protons attached to a particular carbon can be observed from the proton-carbon correlation map. The spectrum also could be used to assign the location of individual deuterium in the ions which results from rearrangement. For example, the contour diagram of this spectrum clearly reveals that the proton absorption at 0.2 ppm is correlated with C_5 as a result of the *exo*-5 to *anti*-7 rearrangement.

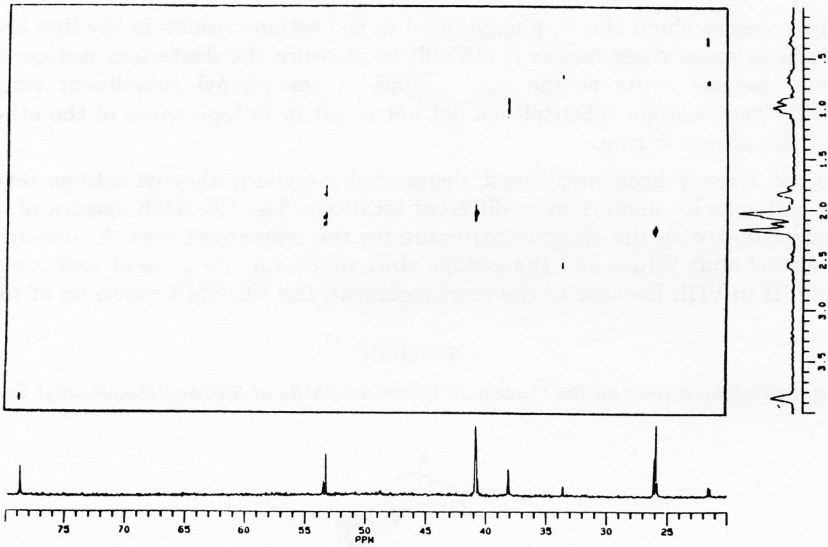


Figure 2. The 2D-COSY spectrum of 2-methyl-2-norbornyl-*exo,exo*-5,6-d_2 cation.

2-Aryl-2-norbornyl Cation

For a series of stable 2-aryl-2-norbornyl cations, we were able to show using ^{13}C NMR spectroscopy the onset of nonclassical stabilization by varying the substitution on the phenyl ring. The deuterium isotope effect changes in this study were relatively small. The application of this method to the ^{13}C NMR spectroscopic study of a series of ring-substituted 2-phenyl-2-norbornyl cations gives evidence for significant differences in deuterium isotope effects. The 2-aryl-2-norbornyl cations are conjugatively more stable than the 2-methyl-2-norbornyl cations. In order to examine the effects of substitution of the phenyl group on the ^{13}C NMR chemical shifts, we compared the ^{13}C chemical shifts of a series of variously deuterated substituted-phenyl-2-norbornyl cations. Generally, those substituent groups vary from the most electrons withdrawing

3,5-$(CF_3)_2$ to the electron releasing *p*-OCH_3 groups. The ^{13}C NMR data for these ions are given in Tables III through VIII. Chemical shift assignments were made on the basis of previous report.

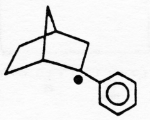
In these cations the positive charge at C_2 is shared with the aromatic ring resulting in increased shielding at the carbocation center and in upfield shifts. The cationic carbon, C_2, is more deshielded in the ions with the electron withdrawing *p*-CF_3 and 3,5-$(CF_3)_2$ substituents than in the ions with electron releasing substituent groups. The introduction of deuterium at the *exo*-6, *endo*-6, or 1 positions results in a downfield isotope shift. The more electron withdrawing the substituent on the phenyl group, the more deshielded is the carbocation center and the more downfield is the deuterium isotope shift at the cationic center. For example, the isotope shift of *exo,exo*-5,6,-dideuterio-4-trifluoromethylphenyl-2-norbornyl cation is 0.47 ppm downfield at C_2. On the other hand, the similar *exo,exo*-5,6-dideuterio-4-methylphenyl-2-norbornyl cation gives a 0.25 ppm downfield deuterium isotope shift.

The rotation about the C_2-phenyl bond in the cations results in the line broadening which in some cases makes it difficult to measure the deuterium isotope effects. However, isotope shifts at the *ipso*-carbons of the phenyl substituent ring were detected. These isotope substitutions did not result in isotope shifts of the other carbons of the aromatic ring.

As has already been mentioned, deuterated 2-aryl-2-norbornyl cations rearrange to give cations with deuterium in different locations. The ^{13}C NMR spectra of cations were consistent with the assigned structure for the rearranged ions. A comparison of the chemical shift values and the isotope shift values for the pairs of ions are shown in Table III to VIII. Because of the rearrangement, the ^{13}C NMR spectrum of the ions

TABLE III

Deuterium Isotope Effects on the Carbon-13 Chemical Shifts of 2-Phenyl-2-norbornyl Cation[a]



Carbon	Chemical shift, ppm	Isotope Effect, ppm[b]				
		exo,exo-5,6-d_2	*exo,anti*-6,7-d_2	*exo*-6-*d*	*endo*-6-*d*	1-*d*
C1	58.100	−0.084	−0.048	−0.040	−0.040	−0.143
C2	259.225	0.291	0.336	0.281	0.105	0.062
C3	49.252	0.0	0.0	0.0	0.0	0.0
C4	38.499	−0.100	−0.100	0.0	0.0	0.0
C5	24.262	−0.406	−0.137	−0.093	−0.093	0.0
C6	33.009	−0.356	−0.356	−0.221	−0.221	−0.124
C7	40.246	0.0	−0.279	0.0	0.0	0.0
C_i[c]	132.231	0.044	0.044	−0.036	0.0	−0.036

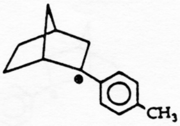
[a] Acquired on an Bruker AM-360 NMR spectrometer at 90.6 MHz and at −90 °C. The chemical shift given is that of the nondeuterated compound to acetone-d_6.

[b] Isotope shifts in the aryl group were not observed except C_i.

[c] C_o 140.339, 139.656; C_m 131.349, 131.157; C_p 151.159

TABLE IV

Deuterium Isotope Effects on the Carbon-13 Shifts of 2-(4-Methylphenyl)-2-norbornyl Cation[(a)]

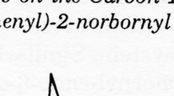


		Isotope Effect, ppm[(b)]				
Carbon	Chemical shift, ppm	*exo,exo*-5,6-d_2	*exo,anti*-6,7-d_2	*exo*-6-*d*	*endo*-6-*d*	1-*d*
C1	56.281	–0.048	–0.091	0.0	0.0	0.0
C2	252.164	0.248	0.248	0.194	0.048	–0.04
C3	48.479	0.0	0.0	0.0	0.0	0.0
C4	38.444	–0.100	–0.100	–0.086	0.0	0.0
C5	25.176	–0.401	–0.141	–0.094	–0.094	0.0
C6	32.447	–0.337	–0.337	–0.298	–0.298	–0.124
C7	40.675	–0.028	–0.263	0.0	0.0	0.0
C_i[(c)]	131.341	0.036	0.036	0.035	0.0	0.035

(a) Acquired on a Bruker AM-360 NMR spectrometer at 90.6 MHz at –90 °C. The chemical shift given is that of the nondeuterated compound relative to acetone-d_6.
(b) Isotope shifts in the aryl group were not observed except C_i.
(c) C_o 141.291; 140.741; C_m 133.129; 132.886; C_p 170.058; CH_3 23.904.

TABLE V

Deuterium Isotope Effects on the Carbon-13 Chemical Shift of 2-(p-Fluorophenyl)-2-norbornyl Cation[(a)]

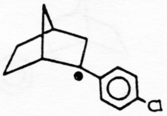


		Isotope Effect, ppm[(b)]				
Carbon	Chemical shift, ppm	*exo,exo*-5,6-d_2	*exo,anti*-6,7-d_2	*exo*-6-*d*	*endo*-6-*d*	1-*d*
C1	47.192	–0.046	–0.046	–0.044	–0.069	–0.069
C2	254.147	0.290	0.322	0.234	0.108	0.054
C3	48.657	0.0	0.038	0.038	0.0	0.0
C4	38.228	–0.100	–0.100	0.0	0.0	–0.085
C5	24.223	–0.413	–0.111	–0.098	–0.098	0.0
C6	32.315	–0.368	–0.368	–0.289	–0.289	–0.126
C7	40.162	0.0		0.0	0.0	0.0
C_i[(c)]	129.357	0.033	0.033	0.04	0.016	0.016

(a) Acquired on a Bruker AM-360 NMR spectrometer at 90.6 MHz at –90 °C. The chemical shift given is that of the nondeuterated compound relative to acetone-d_6.
(b) Isotope shifts in the aryl group were not observed except C_i.
(c) C_o 145.061 (14.5 Hz), 144.462; C_m 119.6885 (22.7 Hz), 119.4370; C_p 176.9165 (288.1 Hz)

TABLE VI

Deuterium Isotope Effects on the Carbon-13 Chemical Shifts of 2-(p-Chlorophenyl)-2-norbornyl Cation$^{(a)}$



Carbon	Chemical shift, ppm	Isotope Effect, ppm$^{(b)}$				
		exo,exo-5,6-d_2	*exo,anti*-6,7-d_2	*exo*-6-*d*	*endo*-6-*d*	1-*d*
C1	57.805	–0.049	–0.049	0.0	0.0	–0.045
C2	256.029	0.322	0.322	0.265	0.064	0.064
C3	48.914	0.0	0.0	0.0	0.0	0.0
C4	38.311	–0.101	–0.101	0.0	0.0	0.0
C5	24.028	–0.399	–0.118	–0.093	–0.093	0.0
C6	32.741	–0.367	–0.367	–0.272	–0.272	–0.132
C7	40.101	0.0		0.0	0.0	0.0
$C_i^{(c)}$	130.321	0.039	0.039	0.0	0.0	0.0

(a) Acquired on a Bruker AM-360 NMR spectrometer at 90.6 MHz and at –90 °C. The chemical shift given is that of the nondeuterated compound relative to acetone-d_6.

(b) Isotope shifts in the aryl group were not observed except C_i.

(c) C_o 140.688, 140.031; C_m 131.736, 131.543; C_p 159.940

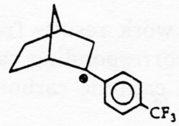
from ionization of the 2-aryl-2-norbornyl-*exo,exo*-5,6-d_2 alcohols gave two peaks for the cationic carbon. The difference in chemical shift for those is smaller than for the corresponding 2-methyl-2-norbornyl system. Similarly, the ^{13}C NMR spectrum of the ions from ionization of the 2-aryl-2-norbornyl-*endo*-6-d_1 alcohols should also give two peaks of the cationic center: one peak for the *endo*-6-d_1 cation and another peak for the 1-d_1 cation. The fact that only one peak was observed for some of the ions means the difference of isotope shifts between the two cations was too small to detect. Thus, both the ions were assigned the same deuterium isotope shifts when they only show one peak in the ^{13}C NMR spectrum.

Olah has reported[23] the effect of substitution in the phenyl ring of 2-phenyl-2-norbornyl cations on the chemical shift of C_1 and C_3, and has shown that the data demonstrate that the onset of non-classical σ-delocalization. Our objective in the present study was to probe the effect of the onset of σ delocalization in 2-phenyl-2-norbornyl cations on the deuterium isotope shifts resulting from deuteration at the C-6 and C-1 positions.

For substituted 2-aryl-norbornyl cations a fair correlation between the deuterium isotope shifts of the cationic carbon and the sigma constant σ^{c+} has been observed. If the isotope shifts of the 4-(trifluoromethyl)phenyl and 3,5-bis(trifluoromethyl)phenyl substituents are disregarded, an excellent linear correlation is obtained. The 4-(trifluoromethyl)phenyl and 3,5-bis(trifluoromethyl)phenyl groups are the most common electron-withdrawing substituent groups used in stable ion studies. The results are entirely consistent with the onset of σ bridging in the norbornyl cation (Figure 3 through 7). The correlation with the σ^{c+} scale is the result of the enhanced shifts for the aryl

TABLE VII

Deuterium Isotope Effects on the Carbon-13 Chemical Shifts of 2-(p-Trifluoromethylphenyl)-2-norbornyl Cation(a)



Carbon	Chemical shift, ppm	Isotope Effect, ppm(b)				
		exo,exo-5,6-d_2	*exo,anti*-6,7-d_2	*exo*-6-*d*	*endo*-6-*d*	1-*d*
C1	62.809	–0.057	–0.085	–0.048	–0.048	–0.011
C2	263.664	0.467	0.565	0.495	0.127	0.076
C3	51.154	0.0	0.0	0.033	0.0	0.0
C4	40.044	–0.098	–0.098	0.0	0.0	0.0
C5	23.950	–0.405	–0.130	–0.091	–0.091	0.0
C6	35.719	–0.285	–0.285	–0.464	–0.326	–0.107
C7	40.548	0.0	–0.300	0.0	0.0	0.0
C_i(c)	133.063	0.045	0.045	0.0	0.0	0.0

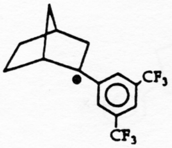
(a) Acquired on a Bruker AM-360 NMR spectrometer at 90.6 MHz and at –90 °C. The chemical shift given is that of the nondeuterated compound relative to acetone-d_6.

(b) Isotope shifts in the aryl group were not observed except C_i.

(c) C_o 139.738, 138.746; C_m 127.557, 127.557; C_p 146.0805 (33.96 Hz); CF_3 121.6255 (273.7 Hz).

TABLE VIII

Deuterium Isotope Effects on the Carbon-13 Chemical Shifts of 2-[3,5-Bis(trifluoromethyl)phenyl]-2-norbornyl Cation(a)



Carbon	Chemical shift, ppm	Isotope Effect, ppm(b)				
		exo,exo-5,6-d_2	*exo,anti*-6,7-d_2	*exo*-6-*d*	*endo*-6-*d*	1-*d*
C1	65.329	–0.060	–0.060	–0.047	–0.047	
C2	261.938	0.595	0.723	0.645	0.179	0.060
C3	51.478	0.091	0.091	0.127	0.033	0.033
C4	40.777	–0.093	–0.093	–0.077	0.0	0.0
C5	23.731	–0.382	–0.121	–0.083	–0.083	0.0
C6	37.297	–0.225	–0.225	–0.174	–0.174	–0.043
C7	40.583	0.0	–0.250	0.0	0.0	–0.127
C_i(c)	130.953	0.049	0.049	0.050	0.0	0.0

(a) Acquired on a Bruker AM-360-NMR spectrometer at 90.6 MHz and at –90 °C. The chemical shift given is that of the nondeuterated compound relative to acetone-d_6.

(b) Isotope shifts in the aryl group were not observed except C_i.

(c) C_o 137.0605; C_m 133.9005 (35.6 Hz); C_p 139.183; CF_3 121.188 (273.1 Hz).

substituents which have been related to the resonance interaction with a π-electron system. This is consistent with this aryl group as a π-electron donor and stabilization of the carbocation. The good correlation with substituent parameters does show that the origin of the isotope shifts is electronic in origin.

An additional aspect of our work results from consideration of the isotope shift of the cationic carbons *vs.* the corresponding carbon-13 chemical shifts. Plots of the deuterium isotope effects at the cationic carbon against the ^{13}C chemical shifts are shown in Figures 8 through 12.

Thus the tool of increasing electron demand also reveals the onset of nonclassical σ-delocalization in these 2-aryl-2-norbornyl cations. In contrast to the linear behavior observed in 2-aryl-2-propyl cations, a plot of the cationic carbon chemical shifts of the 2-aryl-2-norbornyl cations *vs.* the deuterium isotope effects at this carbon shows a linear behavior over only a limited range of substituents. The distinct break that is seen with the electron-withdrawing 4-(trifluoromethyl)phenyl and 3,5-bis(trifluoromethyl)phenyl substituents indicates the onset of σ-delocalization. Excellent correlation coefficients are observed with only the electron releasing substituents included in the analysis. It is known that cationic carbon chemical shifts depend on the electron density at the cationic carbon and the charge delocalization of the cations. The good correlation of deuterium isotope effects with carbon-13 shifts indicates that the correlation may be important in determining the magnitude of the deuterium isotope effects. It is evident, from all the correlations shown in the figures, that the deuterium isotope effects seen in these cations are particularly sensitive to substituents. The isotope shifts change in the expected direction; that is, electron donor substituents shield the cationic nucleus, resulting in a chemical shift to higher field and with relatively smaller isotope shifts.

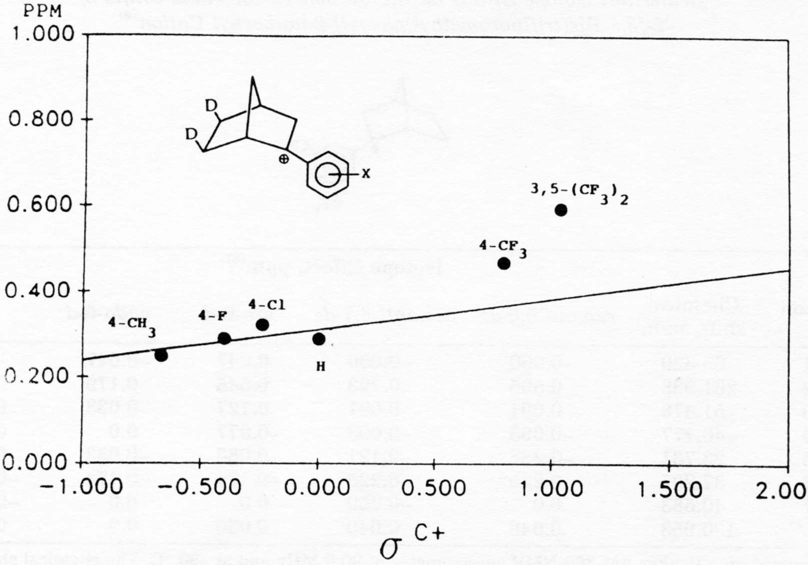


Figure 3. The deuterium isotope effects at cationic carbon C$_2$ *vs.* σ^{c+} for a series of substituted 2-aryl-2-norbornyl-*exo,exo*-5,6-d_2 cations.

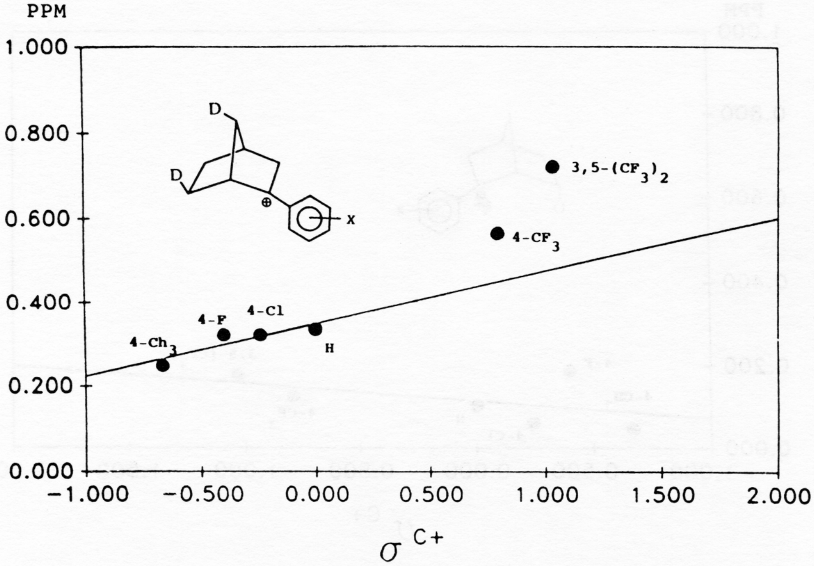


Figure 4. The deuterium isotope effects at cationic carbon C2 *vs.* σ^{c+} for a series of substituted 2-aryl-2-norbornyl-*exo, anti*-6,7-d_2 cations.

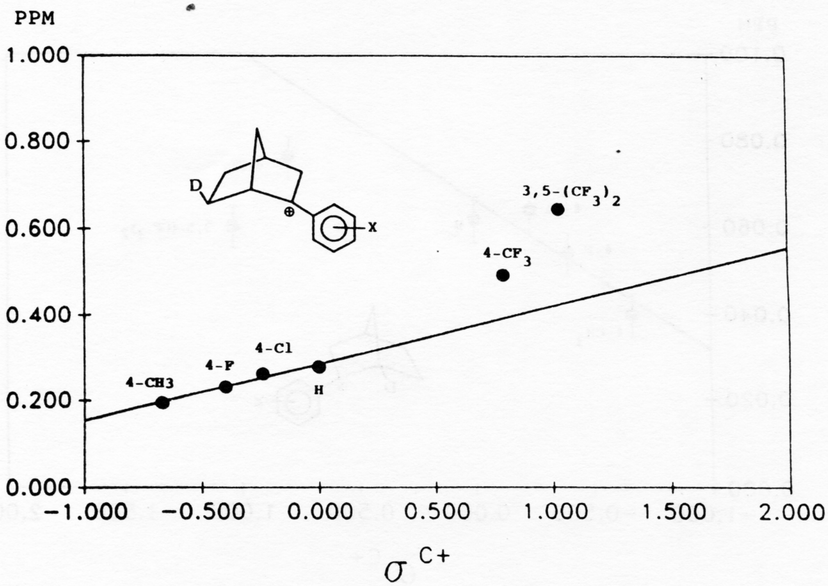


Figure 5. The deuterium isotope effects at cationic carbon C2 *vs.* σ^{c+} for a series of substituted 2-aryl-2-norbornyl-*exo*-6-d_1 cations.

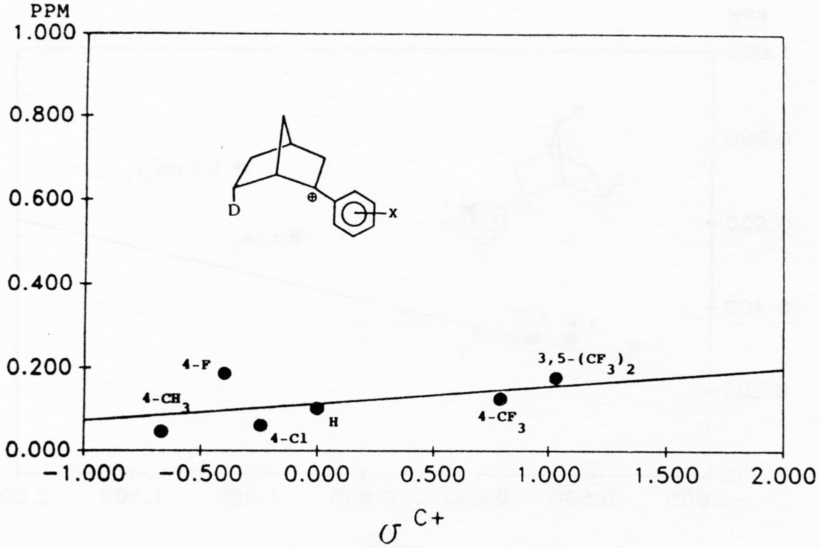


Figure 6. The deuterium isotope effects at cationic carbon C2 *vs.* σ^{c+} for a series of substituted 2-aryl-2-norbornyl-*endo*-6-d_1 cations.

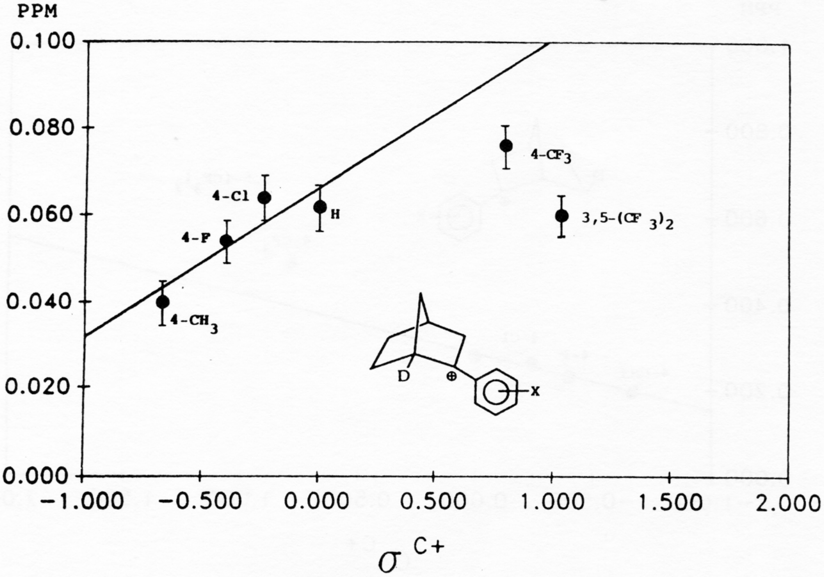


Figure 7. The deuterium isotope effects at cationic carbon C2 *vs.* σ^{c+} for a series of substituted 2-aryl-2-norbornyl-1-d_1 cations.

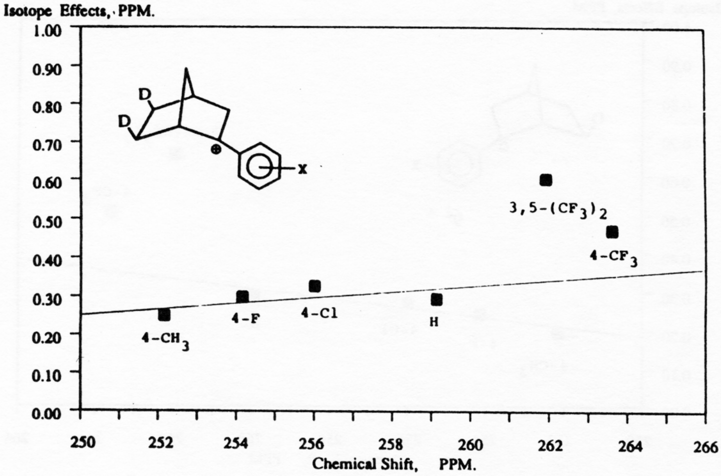


Figure 8. ^{13}C NMR chemical shift at cationic center C_2^+ *vs.* deuterium isotope shift for the cationic carbons of *exo,exo*-5,6-d_2 cations.

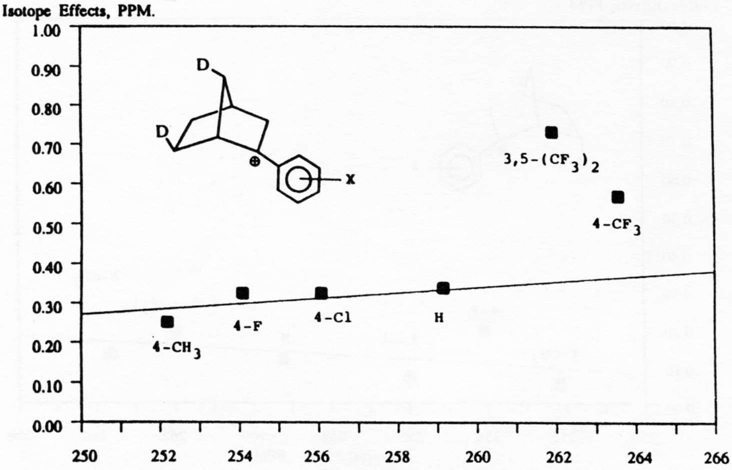


Figure 9. ^{13}C NMR chemical shift at cationic center C_2^+ *vs.* deuterium isotope shift for the cationic carbons of 6,7-*exo,anti*-d_2 cations.

As shown in the figures, the carbon-13 chemical shifts of the cation carbon cover a range of 10 ppm. For example, the ^{13}C chemical shifts of C_2^+ is 252.2 ppm for 4-CH_3-cation and 262.0 ppm for 3,5-(CF_3)-cation. Generally, plots of isotope effects *vs.* δ C_2^+ values give a reasonable linear relationship. It thus appears that the electron requirement of the cationic center are correlated with the deuterium isotope effects. Electron withdrawing groups decrease the delocalization by the phenyl ring and thus enhance the deshielding effect at the cationic carbon. Neighboring σ-bond participa-

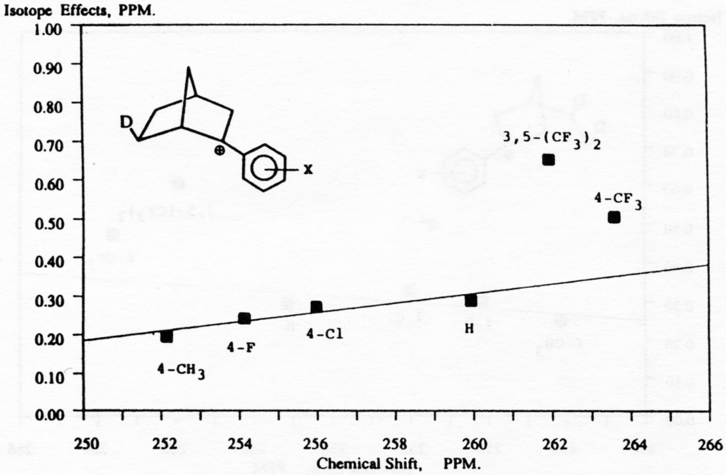


Figure 10. ^{13}C NMR chemical shift at cationic center $C_2{}^+$ *vs.* deuterium isotope shift for the cationic carbons of *exo*-6-d_1 cations.

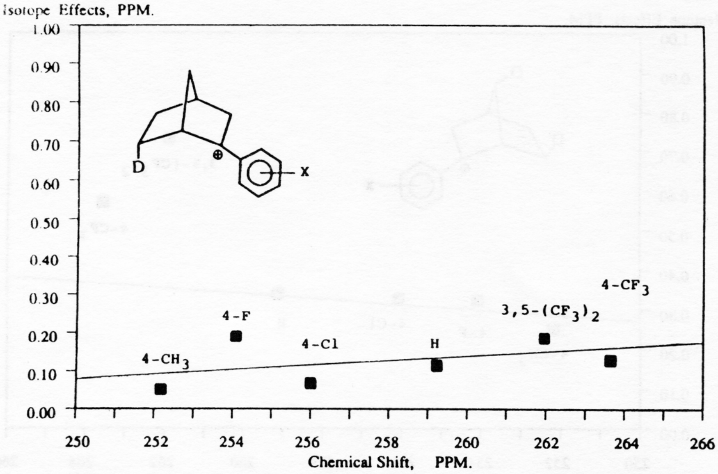


Figure 11. ^{13}C NMR chemical shift at cationic center $C_2{}^+$ *vs.* deuterium isotope shift for the cationic carbons of *endo*-6-d_1 cations.

tion in the ions bearing strong electron withdrawing substituents on the phenyl ring results in charge delocalization into the neighboring C1–C6 σ bond.

EXPERIMENTAL

Unless otherwise specified, all solvents and reagents employed were obtained from Aldrich and used as supplied. Diethyl ether was distilled from sodium benzophenone ketyl under argon just prior to use. Deuterium oxide was purchased from the NSF Isotopes Company. Most reactions were run under inert atmospheres (N_2 or Ar) with use of oven-dried glassware.

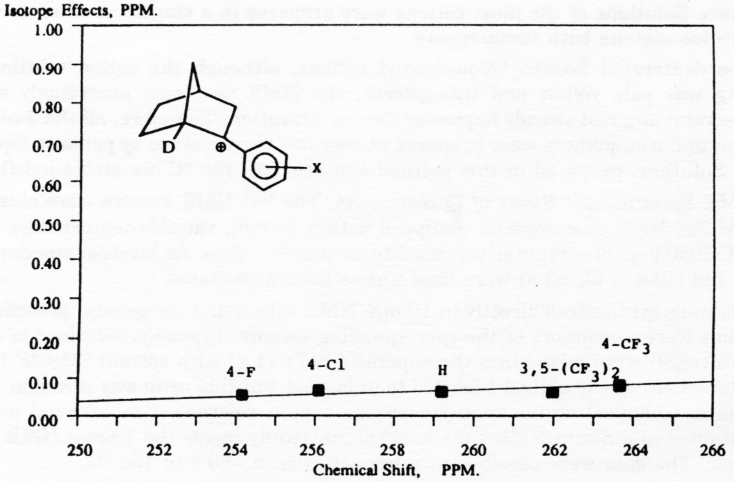


Figure 12. ^{13}C NMR chemical shift at cationic center C_2^+ *vs.* deuterium isotope shift for the cationic carbons of 1-d_1 cations.

^1H NMR spectra were recorded on a Brucker AM-360 NMR spectrometer. GC analyses were performed on a HP-5790 chromatography equipped with a HP-3390A integrator. Column chromatography was performed with silica gel from Merck. Melting points are uncorrected and were taken in open capillaries.

^{13}C NMR measurements were mostly performed on Brucker AM-360 NMR spectrometer using standard operational procedure. A few of the ^{13}C NMR spectra were obtained on an IBM WP-270 SY instrument. All the variable temperature (low temperature) studies were performed on the Brucker AM-360 which was equipped with a thermocouple. In measuring low-temperature ^{13}C NMR spectra, the temperature, digital resolution, and choice of reference are of concern. The reported temperatures are through to be accurate to within ±1 °C.

The digital resolutions were 1.22 Hz/data point for room temperature sample study, and 0.85 Hz/data point for low temperature carbocation study. The reference in normal room temperature case is $CDCl_3$ (taken as δ 77.0 ppm), and in low-temperature case is acetone-d_6 (taken as δ 29.8 ppm) which was contained in a 5 mm NMR tube held concentrically within the 10 mm NMR tube. Spectra below −100 °C were obtained unlocked with no external reference. Peak assignments, with the aid of off-resonance spectra and some references, were relatively easy.

The 2D HXCORR spectrum was acquired on the Brucker AM-360 spectrometer over a 24 hour period at 200 K with the standard HXCORR sequence. The number of data points in the F1 dimension was set equal to 512, while the number of data points in the F2 dimension was 4K. The data set was weighted by a Gaussian multiplication function before 2D Fourier transformation.

Preparation of Carbocations. The most commonly used method of carbocation generation involved direct addition of the precursor dissolved in SO_2ClF to the precooled superacid as used by Olah and coworkers.

Various carbocations can be generated from their corresponding precursors in a superacid system. Typical of the experimental procedures used is that for the carbocation in SbF_5–SO_2ClF solution. A saturated solution of freshly distilled SbF_5 in SO_2ClF is prepared and cooled to −78 °C in a dry ice-acetone bath. To this solution is added, with continuous vigorous stirring using a vortex type stirrer, the alcohol precursor to give an approximately 10% carbocation solution. The solutions obtained after vigorous stirring were clear, with a color ranging from pale yellow to dark brown. Solutions of the most cations were prepared in a similar manner and were fairly stable at dry ice-acetone bath temperature.

For the deuterated 2-methyl-2-norbornyl cations, although the cation solutions obtained after mixing was pale yellow and transparent, the NMR spectrum accordingly showed that deuterium scrambling had already happened during ionization. Therefore, all the 2-methyl-2-norbornyl cation and isotopomers were prepared at very low temperature by pentane-liquid nitrogen slush bath. Solutions prepared in this method and kept at –130 °C are stable indefinitely.

^{13}C NMR Spectroscopic Study of Carbocations. The ^{13}C NMR spectra were obtained with a Brucker AM-360 NMR spectrometer equipped with a 10 mm, variable-temperature ^{1}H-^{13}C dual probe. An ASPECT 3000 computer was used to accumulate data. As internal standards, acetone-d_6 (δ 29.8) and CD_2Cl_2 (δ_c 53.8) were used unless otherwise stated.

All ions were synthesized directly in 10 mm NMR tube using the general procedures. In this work, alcohols were precursors of the corresponding cations. Typically, solutions of the alcohols (100 mg of alcohol) were mixed into the superacid SbF_5 (1 g) with solvent SO_2ClF (2 mol). The ratio of isotopomers was usually 2:1 labeled to unlabeled, but this ratio was varied in some repeat measurements. Chemical shifts were measured in ppm referenced to external acetone-d_6 or CD_2Cl_2 contained in a 5-mm NMR tube held concentrically inside the 10-mm NMR tube with a Teflon spacer. The data were obtained at a temperature of –80 ° to 130 °C.

Cation Precursor. Although alkyl halides and alkyl alcohols were used as precursors in earlier reports, the greater availability of alcohols has resulted in their more convenient use as precursors for cation generation.

Precursor alcohols were prepared by the standard Grignard reactions of the corresponding ketones. 2-Norbornanone was commercially available (Aldrich). Deuterated 2-norbornanone were prepared according to literature procedures.[15-19]

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SAŽETAK

Deuterijski izotopni efekti na ^{13}C pomake 2-supstituiranih 2-norbornil-kationa

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Izmjereni su deuterijski izotopni efekti na ^{13}C kemijske pomake različitih izotopomera 2-metil- i 2-aril-2-norbornil-kationa i prodiskutirana njihova elektronska struktura. Iz izmjerenih pomaka autori zaključuju da 2-metil-2-norbornil-kation ima premoštenu strukturu u otopini, dok rezultati za 2-aril-norbornil kation upućuju na početak stvaranja premoštenja.