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Supplementary Material Available: ^{13}C chemical shifts for **4a-f** and **5a-f** are provided for comparison with previous studies²⁹ (2 pages). Ordering information is given on any current masthead page.

Large Intrinsic Nuclear Magnetic Resonance Isotope Shifts Associated with Bending Motion along the Bridging Coordinate in Carbocations

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Abstract: Deuterium isotope effects on the ^{13}C NMR chemical shifts have been determined for the 2-methyl-2-bicyclo[2.2.2]octyl and 2-methyl-2-bicyclo[2.2.1]heptyl cations. These tertiary carbocations have isotope shifts that are larger than 1 ppm per deuterium, which is an order of magnitude larger than ordinary intrinsic shifts found in nonionic model compounds and in other carbocations. For deuteration at the C_3 methylene or methyl group, the same pattern occurs in both cations: isotope shifts that are large and upfield at C_2 , downfield at C_1 , and upfield at the remaining carbon directly bonded to C_2 . The similarity in the pattern of the isotope shifts suggests that the force field and shielding influences in both ions are similar. The specific results are interpreted as indicating the presence of a shallow potential surface for the bending motion along the direction associated with σ -bridging. Since the existence of the shallow potential does not depend on the actual extent of bridging, the magnitude of the isotope effect is not proportional to the extent of bridging.

Typical intrinsic isotope effects on ^{13}C NMR chemical shifts (the isotope shift, $^n\Delta\text{C}(\text{D})$) are upfield displacements of a few tenths of a ppm per deuterium at the carbon bearing the deuterium and smaller effects at the next carbon and more remote positions.^{2,3} NMR isotope shifts have been especially valuable in distinguishing equilibrium processes from resonance phenomena in structural studies of carbocations.^{4,5} Isotopic perturbation of rapid degenerate equilibria in carbocations typically produces large, temperature-dependent $\Delta\text{C}(\text{D})$ while isotopic substitution in a static species gives small, intrinsic $\Delta\text{C}(\text{D})$. However, in nonequilibrating cations with σ -delocalized structures, isotopic perturbation produces relatively large intrinsic shifts.⁶ In further exploration of intrinsic isotope shifts in carbocations, we now report additional two-bond isotope shifts, $^2\Delta\text{C}(\text{D})$, which are larger than 1 ppm per deuterium in "static" tertiary carbocations. While these $^2\Delta\text{C}(\text{D})$ are smaller than typical equilibrium isotope shifts in carbocations, they are an order of magnitude larger than and of opposite sign to intrinsic shifts in other nonequilibrating carbocations. These unusual isotope shifts indicate a response to isotopic

substitution which appears to differ from both the usual equilibrium and intrinsic effects in carbocations.

Unusually large, upfield isotope shifts resulting from β -deuteration are found at the cation center in the 2-methyl-2-bicyclo[2.2.2]octyl cation (**1**) and the 2-methyl-2-bicyclo[2.2.1]heptyl cation (**2**). Previously, Servis and Shue found upfield $^2\Delta\text{C}(\text{D})$



in static carbocations capable of nonclassical σ - or π -bridging: the "methylcyclobutyl" cation, 7-methyl-7-norbornenyl cation, and **2**.⁶ The $^2\Delta\text{C}(\text{CD}_3)$ at the cation center due to methyl deuteration in these carbocations were notable relative to typical intrinsic effects in being larger than a few tenths of a ppm and being upfield rather than downfield. The upfield $^2\Delta\text{C}(\text{D})$ were ascribed to isotopic perturbation of resonance which increases the relative contribution of the canonical forms that involve bonding to the cation center from the bridging atom. In contrast, downfield $^2\Delta\text{C}(\text{D})$ were observed for classical static carbenium ions such as the 2-methyl-2-propyl, 2-methyl-2-butyl, and 1-methylcyclopentyl cations. The downfield $^2\Delta\text{C}(\text{D})$ at C^+ apparently originate from reduced hyperconjugative electron release from C-D bonds relative to C-H bonds,⁶ an interpretation which has been supported by similar findings in several other studies.⁷⁻¹⁰ The contrasting

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Table I. ^{13}C NMR Isotope Shifts^a in Isotopomers of **1**

compd	<i>T</i> , °C	C ₁	C ₂	C ₃	C ₄	C _{5,7}	C _{6,8}	CH ₃
1a	-100	0.45	-1.49	-0.31	0.18	0.00	0.00	<i>b</i>
1a	-82	0.45	-1.40	-0.27	0.14	0.00	0.00	<i>b</i>
1a	-63	0.44	-1.34	-0.21	0.15	0.00	0.00	<i>b</i>
1b	-133	1.01	-2.96	<i>b</i>	<i>c</i>	0.00	<i>c</i>	-0.33
1b	-123	0.98	-2.81	<i>b</i>	0.11	0.00	0.14	-0.30
1b	-113	0.93	-2.64	<i>b</i>	0.10	0.00	0.15	-0.30
1c,d	-110	-0.10	0.44	0.09	0.00	0.10	<i>b</i>	0.06
			0.55					

^aIn ppm, ± 0.01 ppm. Positive sign indicates a downfield shift in the deuterated ion. ^bNot observed because of weak signal for the multiplet of the labeled carbon. ^cNot observed because of viscosity line broadening.

Table II. ^{13}C NMR Isotope Shifts^a in Isotopomers of **2** and **3**

compd	<i>T</i> , °C	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	CH ₃
2a	-98	0.49	-2.26	-0.35	<i>b</i>	-0.06	-0.10	-0.09	<i>c</i>
2a	-78	0.48	-2.17	-0.34	-0.04	-0.07	-0.10	-0.09	<i>c</i>
2a	-58	0.43	-2.09	-0.31	-0.04	<i>d</i>	<i>d</i>	<i>d</i>	<i>c</i>
2a	-38	<i>d</i>	-2.02	-0.32	-0.02	<i>d</i>	<i>d</i>	<i>d</i>	<i>c</i>
2b	-90	0.67	-2.51	-0.9	-0.23	0.00	0.12	-0.20	-0.22
3^e	20	0.00	0.10	-0.68	-0.19	-0.08	0.01	-0.06	

^aIn ppm, ± 0.01 ppm. Positive sign indicates downfield isotope shift. ^bNot observed because of viscosity line broadening. ^cNot observed because of weak signal for the multiplet of the labeled carbon. ^dNot observed because of exchange-broadened lines. ^eIn CDCl₃.

Table III. Temperature Dependence of ^{13}C Chemical Shifts^a for **1** and **2**

compd	<i>T</i> , °C	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	CH ₃
1	-102	65.6	322.2	58.1	35.0	22.9	29.7		38.6
1	-82	66.2	321.6	58.2	35.4	23.1	30.0		38.7
1	-63	66.7	321.2	58.3	35.8	23.3	30.4		38.7
2	-98	79.4	269.2	54.1	41.7	22.5	34.2	39.0	27.0
2	-78	79.7	269.6	54.4	41.9	22.7	34.6	39.2	27.2
2	-58	80.0	270.0	54.7	42.0	22.8	34.9	39.4	27.3
3	20	49.8	217.7	45.2	35.2	27.2	24.2	37.6	

^aIn ppm from tetramethylsilane, referenced to internal CH₂Cl₂ at 53.62 ppm.

behavior led Servis and Shue to suggest that isotope shifts could be used as an independent tool for differentiating carbocations with different charge delocalization mechanisms.⁶ Indeed, intrinsic shifts have proven useful in probing structure and electron distribution in carbocations and other molecules.¹⁰⁻¹²

Both **1** and **2** display a similar pattern of isotope shifts, suggesting a common origin for the isotope shift. However, on the basis of chemical shift criteria, **1** has usually been considered a classical, nonbridged cation while **2** has been considered a partially bridged cation.^{6,13} Thus, an interpretation based on isotope shifts that **1** has a three-center, two-electron bond would be in apparent contradiction with the previous conclusion based on carbon chemical shifts that **1** has a classical structure. Examination of this apparent contradiction leads to a more detailed understanding of the origin of intrinsic isotope shifts associated with nonclassical σ -bridging.

Results

NMR isotope shifts at ^{13}C nuclei are given in Table I for the 2-(methyl-*d*₃)-2-bicyclo[2.2.2]octyl cation (**1a**) and the 2-methyl-2-bicyclo[2.2.2]octyl-3,3-*d*₂ cation (**1b**). Isotope shifts at the cation center are shown in Figure 1. In Table II are listed $\Delta\text{C}(\text{CD}_3)$ for methyl deuteration in the 2-(methyl-*d*₃)-2-bicyclo[2.2.1]heptyl cation (**2a**) measured at higher field than for the previously reported results.⁶ Some of the isotope shifts important for later discussion are shown with the structures. These isotope shifts were measured at 75.4 MHz on a Varian XL-300 spectrometer, in each case from a solution containing a mixture of the labeled and unlabeled ion. Results for 2-methyl-2-bicyclo[2.2.1]heptyl-3,3-*d*₂ cation (**2b**) are also listed in Table II, but these isotope shifts were measured at 67.9 MHz on an IBM

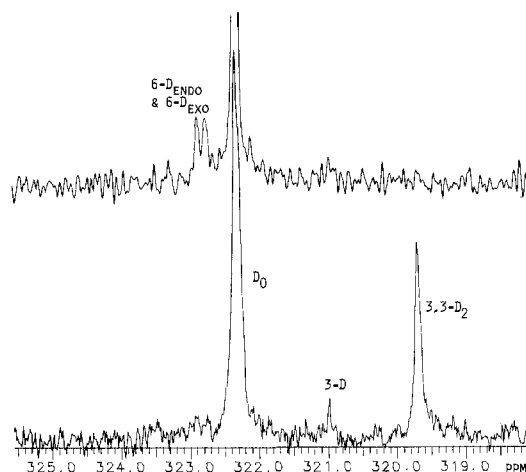


Figure 1. Downfield region showing resonances for the cation center in proton-decoupled 75.4-MHz ^{13}C NMR spectra of isotopomer mixtures of **1**. The lower spectrum contains unlabeled **1** and **1b** and was measured at -113 °C. The upper spectrum was measured at -110 °C for a mixture containing **1**, **1c**, and **1d**.

WP-270 SY NMR spectrometer. Estimated errors in the $\Delta\text{C}(\text{D})$ are about 0.01 ppm, based on the digital resolution. ^{13}C chemical shift data for **1** and **2**, including temperature dependence, are given in Table III and are in good agreement with previous reports.^{14,15}

Carbocations **1a**, **1b**, and **2a**, as mixtures with the unlabeled **1** or **2**, were prepared by dropwise addition of a solution of the corresponding chlorides for **1a** and **1b** or alcohols for **2a** in SO_2ClF to a vortex-stirred solution of 1:1 $\text{FSO}_3\text{H}/\text{SbF}_5$ in SO_2ClF at -78 °C (dry ice-acetone bath) or ca. -130 °C (pentane-liquid N_2 bath). It is necessary to prepare **1b** at low temperature to avoid

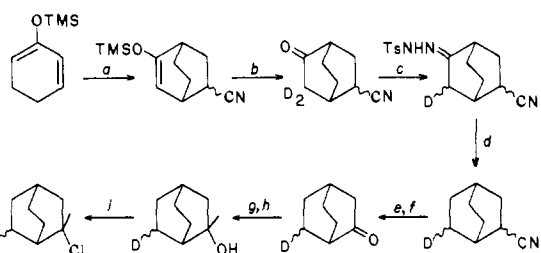
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Scheme 1^a

^a (a) Acrylonitrile (2.5 equiv)/140 °C/toluene/48 h. (b) MeOD/NaOMe/20 °C/24 h. (c) TsNHNH₂ (1.05 equiv)/EtOH reflux/4 h. (d) NaCNBH₃ (4 equiv)/TsOH (0.1 equiv)/1:1 DMF-sulfolane/cyclohexane/110 °C/26 h. (e) PCl₅-pyridine (4 equiv)/CHCl₃ reflux/36 h. (f) KOH (4.25 equiv)/DMSO and H₂O/20 °C/24 h. (g) CH₃MgI (1.25 equiv)/Et₂O/15 h. (h) 2% H₂SO₄ (2.50 equiv). (i) Concentrated aqueous HCl (10 equiv)/minimal CHCl₃/15 min.

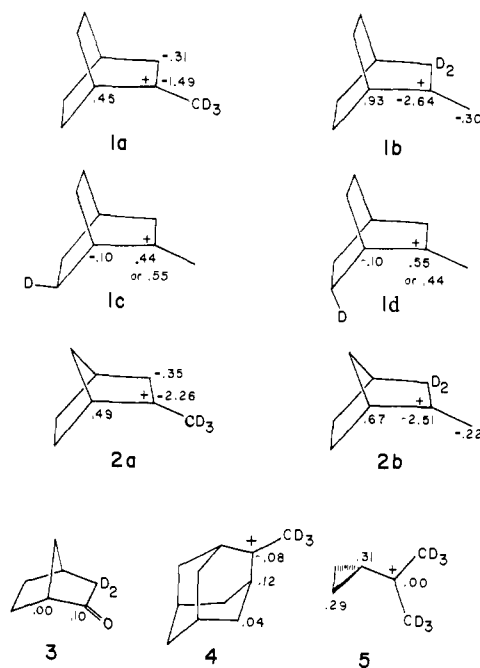
scrambling of the label. If the solution is allowed to warm to about -100 °C, rapid scrambling occurs. A ²H NMR spectrum at -80 °C indicated scrambling of deuterium to all positions in the ring system. The deuterium label also readily scrambles in **2b**. Therefore, this ion was prepared by placing a 2.5:1 mixture of 2-chloro-*endo*-2-methylbicyclo[2.2.1]heptane-3,3-*d*₂ and the unlabeled chloride dissolved in SO₂ClF in a 10-mm NMR tube and freezing this in liquid nitrogen. Small portions of a solution of SbF₅ in SO₂ClF were added to the frozen solution. After each addition, the solution was allowed to thaw slowly with vortex stirring and then refrozen before the next addition. The sample was frozen in liquid nitrogen until the NMR tube was inserted into the NMR probe equilibrated at -90 °C. The spectrum was acquired within 20 min and then reacquired after 60 min had elapsed. The spectra were identical in all respects. The label in ions **1a** and **2a** does not readily scramble, so that isotope shifts could be measured for these ions over a wide temperature range up to ca. -60 °C.

Some isotope shifts were also determined for the C₆-deuterated species **1c** and **1d** and are listed in Table I. The isotopically shifted peaks for the cation center are shown in Figure 1. These ions are available only in a threefold mixture of approximately equal amounts of **1c** and **1d** and about 75% unlabeled **1**. Because of the nature of the mixture, it was not possible to assign isotope shifts to a particular orientation of the deuterium at C₆. However, the two isotopomers are diastereomers and it is clear that two different isotope shifts are observed at C₂. Smaller isotope shifts were observed at some of the other positions, but again it was not possible to make assignments between **1c** and **1d** or to determine whether both gave the same isotope shift.

Ions **1c** and **1d** had to be prepared at -130 °C and NMR spectra were taken at -110 °C to avoid scrambling of the deuterium to other positions. At -80 °C, ¹H and ²H NMR spectra indicated that scrambling to all other ring positions occurs. Cooling again to -110 °C and reacquiring the ¹³C spectrum showed that the peaks due to **1c** and **1d** had diminished in size and small new peaks for other isotopomers were present. For example, a small C₂ peak at -1.3 ppm upfield of the C₂ peak of unlabeled **1** indicated the presence of deuterium at C₃, since this isotope shift is half that of the C₃-*d*₂ isotopomer, **1b**. Ions **1c** and **1d** were prepared from C₆-labeled 2-chloro-2-methylbicyclo[2.2.2]octane, prepared as shown in Scheme I.

As a reference for ordinary isotope shifts, the effects of deuteration at C₃ in 2-norbornanone (**3**) are reported in Table II. Isotope shifts were also determined for methyl deuteration in two additional carbocations: the 2-methyl-2-adamantyl-*d*₃ cation (**4**) and the 2-cyclopropyl-2-propyl-*d*₆ cation (**5**). These were prepared and measured in 1:1 FSO₃H/SbF₅ in SO₂ClF at -78 °C. ¹³C NMR spectra at 75.4 MHz of mixtures with the unlabeled ions gave the isotope shifts shown with the structures in Chart I. Chemical shifts¹⁶ were in good agreement with previous reports.^{13,17}

Chart I



Discussion

Most notable for all of the labeled ions in Tables I and II are the large upfield ²ΔC(D) at the cation center, C₂, and the large downfield ³ΔC(D) at C₁. The ²ΔC(D) is almost -1.5 ppm per deuterium and ³ΔC(D) is 0.5 ppm per deuterium in **1b** at -133 °C. The corresponding isotope shifts in **2b** are nearly as large. Isotope shifts in **1a** and **2a** are less than 1 ppm per deuterium, but still exceptionally large for intrinsic shifts. The highly unusual nature of the isotope shifts in **1** and **2** may clearly be seen by comparison with the isotope shifts for C₃-deuterated 2-norbornanone (**3**) in Table II. In **3**, which is typical of neutral, static species, the ΔC(D) are smaller than |0.10| ppm per deuterium at all positions except the directly labeled C₃, i.e., an order of magnitude smaller than at C₁ and C₂ in **1** and **2**.

Besides C₁ and C₂, the remaining carbon attached to the cation center undergoes an upfield shift in both **1** and **2** when C₃ or the methyl is deuterated. C₃ is shifted upfield in **1a** and **2a**; the methyl carbon is shifted upfield in **1b** and **2b**. Generally smaller isotope shifts are seen at other positions more remote from the cation center, but these do not show any obvious pattern.

The same pattern of isotope shifts at the cation center and adjacent positions occurs in both **1** and **2**: large upfield ²ΔC(D) at C₂, somewhat smaller downfield ³ΔC(D) at C₁, and an upfield ³ΔC(D) at the remaining carbon directly bonded to C₂. The similarity of the response in **1** and **2** suggests a common origin for the isotope shifts. As previously noted for **2a**,⁶ this pattern of isotope shifts is consistent with a perturbation of a σ-delocalized bonding structure toward greater σ-delocalization. Such a perturbation would increase electron density at C₂, decrease electron density at C₁, and decrease hyperconjugative involvement of the C₃ methylene and the methyl group. A recent theoretical study of chemical shifts in carbocations supports previous interpretations that a cationic carbon in a nonclassical structure will be far more shielded than the carbocation center of an open, classical ion.¹⁸

Labeling of **1** at C₆ as in **1c** or **1d** produces a downfield isotope shift of about +0.5 ppm. In a classical structure for **1**, this would be an effect on a center at three bonds distance from the deuterium, ³ΔC(D). As such, the magnitude is as unusual as the effects in **1a** and **1b**. However, in the case of **1c** and **1d**, the isotope effect is deshielding at C₂, which is the opposite of **1a** and **1b** and

(16) Cation **4**: (δ_C, ppm) 322.2, C⁺; 65.7, C_α; 51.9, C_β; 40.7, CH₃; 36.0, C_γ; 28.5, C_γ. Cation **5**: 281.4, C⁺; 56.7, C_α; 53.2, C_β; 38.7, 28.8, CH₃.

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is thus consistent with decreased σ -donation from the C₁-C₆ or C₁-C₈ bond.

Explanations of isotope shifts must ultimately be related to vibrational differences among isotopomers. Equilibrium isotope shifts are simply explained as changes in weighted average chemical shifts when a rapid equilibrium is altered by ordinary isotope effects which arise from differences in vibrational energy content of the equilibrating species. For a single "static" species, isotopic substitution does not change the electronic potential energy surface (Born-Oppenheimer approximation) or fundamental structure; intrinsic NMR isotope shifts must arise from changes in the nuclear shieldings when averaged over the populated vibrational and rotational states which differ among isotopomers. Despite having the same potential energy surface, it is theoretically reasonable that isotopomers actually have different vibrationally averaged geometries because isotopic substitution changes the frequencies and amplitudes of motions within anharmonic energy surfaces.¹⁹

Since the shielding of a nucleus in a molecule is a function of internuclear separation, the isotope effects on chemical shifts could, in principle, be calculated by integrating the nuclear shielding over the vibrational potential surface for the two isotopomers.¹⁹ Such full dynamical calculations of the variation of shielding with internal coordinate have been reported for a few diatomic molecules. While such studies are of fundamental importance in establishing the origin of isotope effects on chemical shifts, they are not readily extended to the polyatomic molecules of general interest.²⁰

Deuterium isotope effects on ¹³C chemical shifts can be modeled by using molecular orbital methods to calculate the change in total atomic charge resulting from a reasonable isotope effect on bond displacement in the C-H bond and assuming the usual charge-shift relationship.^{10,21} The magnitude and directions of the changes in electron density are sufficiently large to account for the magnitude and sign of both the 1-bond and 2-bond chemical shift isotope effects in ketones and classical carbocations. The unusual β -deuterium isotope effects in **1** and **2**, however, cannot be suitably modeled by using fixed structures. MO calculations aimed at simulating the effect of deuterium substitution in **2a**, which was defined with a fully bridged geometry,²² did not show the appropriate changes in electron distribution.^{21a} Similar calculations on **2a** with a partly bridged structure²² showed that deuteration should decrease electron density at the cation center as in other classical cations, including **1a** if it is defined by a symmetrical, unbridged geometry.²³

Calculations carried out so far with this perturbational model of isotope shifts have not attempted to account for changes in average geometry other than at the C-H(D) bonds. In essence, this model considers perturbation of resonance wherein one bond length is perturbed and the remainder of the atoms are fixed in position, so that only the electron distribution changes. Obviously, in molecules where bridging may be important, any isotopically induced changes in the vibrationally averaged geometry of the bridging atoms may also have a substantial effect on shieldings, since carbocation shieldings are very sensitive to geometry.¹⁸ In order to account for the results in bridged systems, it will probably be necessary to use a more complex model in which changes in the average geometry for the whole molecule are considered, and it would obviously be desirable to calculate shieldings directly instead of relying on a relationship with electron densities. Because of the limitation of the model, it is not surprising that the calculations fail for systems with three-center, two-electron bonds.

Ion **1** has generally been considered a purely classical cation, with no σ -bridging. The C⁺ chemical shift is 322 ppm, within

the 330 \pm 10 ppm range considered typical of more than 100 examples of classical aliphatic and cycloalkyl cations.²⁴ Olah et al. did not consider it even a borderline case, based on the criterion of total chemical shift difference relative to a hydrocarbon model.¹³ A study of the 2-bicyclo[2.2.2]octyl system by the "tool of increasing electron demand" showed no anomalous behavior.²⁵ In contrast, the 2-bicyclo[2.2.1]heptyl cations are notorious for displaying nonclassical behavior, including nonlinear correlations in applications of the "tool of increasing electron demand".^{25,26} In the particular instance of **2**, the unusually shielded cationic center at 270 ppm and the criterion of total chemical shift difference relative to a hydrocarbon standard were taken to indicate borderline nonclassical character, i.e., partial σ -bridging.^{6,13} Thus, a conclusion based on isotope shifts that **1** has a three-center, two-electron bond would be in apparent contradiction with the conclusion drawn from the C⁺ chemical shift that **1** has a classical structure. Several possible explanations of the isotope shift behavior were therefore considered and are discussed below.

One possible origin of the isotope shifts is isotope effects on intermolecular interactions. However, if ion-pairing equilibria or solvation were being perturbed, it is difficult to comprehend how such effects could operate in the opposite direction for the *tert*-butyl and 1-methylcyclopentyl cations,⁶ for example, compared to **1** and **2**. Secondary kinetic isotope effects on the formation of ions in solvolysis reactions are consistent across a variety of systems. Furthermore, in a previous study of intrinsic NMR isotope shifts in carbocations, variation in the superacid and counterion had little effect on the isotope shifts.^{10b} Similarly, except for the results reported here for **1** and **2**, most intrinsic shifts in carbocations are not highly sensitive to temperature. On the basis of intermolecular effects, it would also be difficult to explain such features as nonequivalent ortho carbons in the 2-phenyl-2-propyl cation labeled at only one of the methyl groups.¹² Thus, the explanation for the similarity in isotope shift behavior for **1** and **2** and contrast with other carbocation systems is likely to be found in a structural feature and not in intermolecular effects.

One possibility that we considered was that isotope shifts such as those observed for **1** and **2** might be the normal response for carbocations stabilized by C-C hyperconjugation. Previous examples of classical cations displaying downfield isotope shifts at C⁺ of about 0.1-0.2 ppm/deuterium did not have C-C bonds well aligned for hyperconjugation.^{6,21} To test this hypothesis, isotope shifts due to methyl deuteration in **4** and **5** were determined. Both are considered to be static classical carbenium ions, and both have C-C bonds suitably aligned for hyperconjugation with the p orbital at the cation center. The strained cyclopropyl ring is well-known to be an exceptionally good electron donor and such electron donation is thought to be responsible for the unusually shielded cation center in **5**.¹⁵⁻¹⁷

In **4** and **5**, the isotope shifts at C⁺ due to methyl deuteration are very small, unlike the large upfield shifts observed in **1a** and **2a**. Also, downfield isotope shifts are observed for both carbon atoms of the C-C bonds involved in hyperconjugation in **4** and **5**. In contrast, downfield shifts on CD₃ substitution were not observed at C₆ in **2a** or C_{6,8} in **1a** and the downfield ³ Δ C(D) at the C₁ carbons in **1a** and **2a** are much larger than the ³ Δ C(D) in **4** and **5**. It is clear that the isotope shifts observed in **1** and **2** are unlike those of other classical carbenium ions stabilized by C-C hyperconjugation.

Another possibility is that the unusual shifts in **1** and **2** might be due to isotopic perturbation of rapid equilibria with rearranged ions. This hypothesis was discussed and ruled out for **2a** in a previous study.⁶

Nonetheless, it is conceivable that cation **1** might be in rapid equilibrium with any of the cations **6-11**. Consideration of the energetics involved in an equilibrium between **1** and any of these

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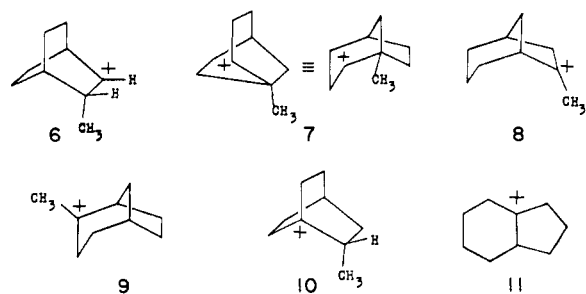
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species leads to their elimination as possibilities. The most likely candidates are the 2-methyl-3-bicyclo[2.2.2]octyl cation (**6**) and the 1-methyl-2-bicyclo[3.2.1]octyl cation (**7**). But these can immediately be ruled out, since these secondary cations should be 5.5–12 kcal/mol higher in energy than tertiary **1**, based on the activation energy for the rearrangement between **1** and the 2-methyl-2-bicyclo[3.2.1]octyl cation (**8**)¹⁴ and on other comparisons of secondary and tertiary ions.²⁷ Altering the energy difference between **1** and **6** or **7** with an isotope effect worth on the order of 150 cal/mol^{4a} would have no observable impact on such lopsided equilibria.

Rapid equilibration with **8** can be ruled out because it is separately observable at temperatures below $-100\text{ }^{\circ}\text{C}$. A rapid equilibrium of **1** with the 6-methyl-6-bicyclo[3.2.1]octyl cation (**9**) can also be ruled out, since this rearrangement would have to go via **7**.²⁸ Rearrangement of **1** to the 2-methyl-1-bicyclo[2.2.2]octyl cation (**10**) is highly unlikely because the $\text{C}_1\text{-H}$ is not suitably aligned for a 1,2-shift and **10** should be much higher in energy. An irreversible rearrangement of **1** to the 1-bicyclo[4.3.0]nonyl cation (**11**) has been observed at temperatures above $-30\text{ }^{\circ}\text{C}$.²⁹

It is therefore apparent that the unusual isotope shifts observed for **1** cannot readily be explained as resulting from isotopic perturbation of an equilibrium between **1** and some other classical cation. However, the fact that both the isotope shifts and chemical shifts for **1** are somewhat temperature dependent, as seen in Tables I and III, makes it attractive to treat the data as though an equilibrium exists, with no preconception of what the second species might be. If **1** is in equilibrium with one other species, the chemical shift observed for the cation center is a weighted average; hence

$$\delta_{\text{obsd}} = x\delta_1 + (1-x)\delta_2$$

where δ_1 and δ_2 are the chemical shifts for this carbon in the two species and x and $1-x$ are the mole fractions of the two forms. The free energy difference between the two forms can be calculated from the equilibrium constant

$$x = (\delta_{\text{obsd}} - \delta_2) / (v_1 - v_2)$$

$$K = x / (1-x)$$

$$\Delta G = -RT \ln K$$

The chemical shifts δ_1 and δ_2 are not known, but the cation chemical shift of **1** as a classical cation should be between the observed 322 ppm and about 340 ppm. Values of ΔG can be calculated by using a variety of values for δ_1 and δ_2 , with the further criterion that the correct pair of δ_1 and δ_2 should give approximately the same values of ΔG at all three temperatures. The isotope effect on the supposed equilibrium, i.e., $\Delta\Delta G$, can then be found by using the pair of δ_1 and δ_2 values and chemical shift data for **1a**.

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(28) Line broadening of the C_1 , C_3 , C_6 , and C_7 resonances was observed in **2** at temperatures above $-75\text{ }^{\circ}\text{C}$ due to a similar rearrangement. No line broadening was observed in the ^{13}C NMR spectrum of **1**. Line broadening has also been observed in the ^1H NMR spectrum of **2**: Huang, E.; Ranganayakulu, K.; Sorensen, T. S. *J. Am. Chem. Soc.* **1972**, *94*, 1780.

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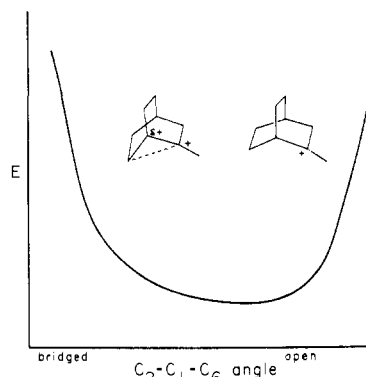
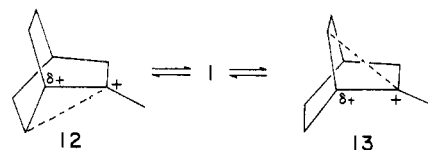


Figure 2. Representation of a potential energy surface for the $\text{C}_2\text{-C}_1\text{-C}_6$ bending motion leading to bridging in cation **1**. The shallow surface would have low-frequency vibrations and thus thermally populated, low-lying excited states. Anharmonicity leads to more bridging at higher temperatures. β -Deuteriation at C_3 or CH_3 would also shift vibrationally averaged structure toward bridging because of zero-point vibrational energies for the higher frequency stretching and bending motions of C-H and C-D bonds. The difference in ZPE between β C-H and C-D bonds is greater for the bridged structure where β C-H(D) bonds are not as weakened by hyperconjugation.

Scheme II



Good agreement of ΔG values for the supposed equilibrium was obtained for many pairs of δ_1 and δ_2 values, with δ_1 between 328 and 340 ppm and δ_2 between 303 and 292 ppm. For example, when $\delta_1 = 332$ ppm and $\delta_2 = 300$ ppm, $\Delta G(\text{CH}_3) = 282 \pm 2$ cal/mol and $\Delta G(\text{CD}_3) = 208 \pm 2$ cal/mol at the three temperatures studied. The free energy change on methyl deuteration in this example is 74 cal/mol, with a range from about 45 to 105 cal/mol for all the suitable pairs of δ_1 and δ_2 . These isotope effects are reasonable compared to the value for the known equilibrating system, 1-(methyl- d_3)-2-methylcyclopentyl cation, of 174 cal/mol.^{4a}

Thus, if the chemical shift and isotope shift data for **1** are treated as arising from a rapid equilibrium between a classical **1** and another species, the second species must be only slightly less stable. Moreover, it is important to note that the highly deshielded ($\delta_{\text{C}} = 340\text{--}328$) carbon at the cationic center in **1** would have to be transformed by the equilibrium into another highly deshielded ($\delta_{\text{C}} = 282\text{--}303$) carbon in the second species. It is difficult to devise any such species other than a partly bridged form of **1**. This possibility is illustrated in Scheme II, wherein a symmetrical **1** would have to be in equilibrium with two partly bridged forms, **12** and **13**, one with bridging by C_6 and the other by C_8 . The two partly bridged forms are enantiomeric unless the pattern of labeling removes the degeneracy. Deuteriation of the methyl group or C_3 methylene would shift the equilibrium toward the bridged forms, since deuterium is found preferentially at nonhyperconjugating positions.⁴ For the same reason, deuteration at C_6 would shift the equilibrium away from **13** toward **1**. It is not clear what sort of isotope effect to expect for deuterium at the bridging atom in **12**.

Despite our analysis that the temperature dependence of the C_2 chemical shifts for **1** can be fit by assuming an equilibrium between two species of similar energy and structure, we prefer a different explanation. Since it is unlikely that a large energy barrier, if any, would exist between very similar structures, and since a large range of paired values of δ_1 and δ_2 give good agreement with the δ_{obsd} data, it seems more reasonable to suggest that there is not an equilibrium but rather a continuum of structures on a relatively flat energy surface for the bending motion along the direction associated with bridging. With a flat energy

surface, the vibrationally averaged geometry could be easily perturbed by isotope effects, or by temperature changes which would change the populations in low-lying vibrational states. The isotope shifts would then be intrinsic rather than equilibrium isotope shifts and are likely to be larger than ordinary intrinsic NMR isotope shifts for systems with narrow potential energy wells where changes in the vibrationally averaged geometry are smaller.

A suggested form for the potential energy surface of **1** as a function of the C₂-C₁-C₆ bond angle is shown in Figure 2. The surface for the bending/bridging motion must be rather flat to accommodate the isotope shift data. The secondary isotope effect due to deuterium substitution at the C₃ methylene or the methyl would favor the more bridged portion of the energy surface because the C₃-H or methyl C-H bonds would be less involved in hyperconjugation and hence would have stronger force constants for their stretching and bending motions.³⁰ Deuteriation at C₆ would favor the less bridged portion of the energy surface. The surface must be anharmonic with the partly bridged end higher in energy to accommodate the direction of the chemical shift temperature dependence at C₂ for **1**. The overall result would be a vibrationally averaged structure for **1** which is slightly bridged.

Besides the upfield shift for C₂ with increasing temperature, the temperature dependence of some of the other ¹³C NMR signals of **1** in Table III is also in agreement with this proposal. Increasing the temperature would increase the population in low-lying vibrational states and thus the vibrationally averaged structure would be shifted toward a more bridged form of **1**. All of the other carbons exhibit downfield shifts with increasing temperature, but C₁ becomes most deshielded, consistent with increased positive charge and decreased bonding at C₁. The C₃ and CH₃ carbons experience the least deshielding with increased temperature, consistent with decreased hyperconjugative involvement of these centers as bridging from C₆ or C₈ increases.

A similar analysis may be applied to the data for **2**. The isotope shift data are again accommodated by suggesting a flat energy surface for the bending motion along the bridging coordinate so that a secondary isotope effect can alter the average C₂-C₁-C₆ bond angle toward more bridging. Although the isotope shift data, including their temperature dependence, are very similar for **2a** and **1a**, the temperature dependence of the chemical shifts for **2** is different. The C₂ cation center in **2** becomes deshielded with increasing temperature, whereas C₂ in **1** becomes more shielded. In the case of **2**, if the C₂ chemical shift is treated as an average value arising from a rapid equilibrium between two species, the partly bridged species must be lower in energy than the more open form. Good agreement of ΔG values at different temperatures and for both labeled and unlabeled forms can be obtained with many pairs of δ₁ and δ₂ values, where δ₁ is between 314 and 340 ppm and δ₂ is between 230 and 203 ppm. The ΔG values range between -20 and -60 cal/mol. The values for ΔΔG are between 25 and 40 cal/mol. However, since all of the carbons in **2** become deshielded with increasing temperature, with C₂ showing only a slightly larger effect than the others, it may be more realistic to simply consider the potential surface to be nearly harmonic with respect to C₂-C₁-C₆ bending, such that temperature would have little effect on the average C₂-C₁-C₆ bond angle. The chemical shift of 270 ppm for C₂ in **2** suggests that the average position on the flat energy surface is a more bridged structure than in **1**, where δ_C for C₂ is 322 ppm.

Conclusions

The similarity of the unusually large isotope shifts for **1** and **2** suggests that the isotope shifts are likely to have a common origin. Considering the vibrational origin of isotope shifts, it is likely that the force field and shielding influences in both ions are similar. On the other hand, the chemical shifts of the cation centers in **1** and **2** differ substantially and the temperature dependence of the chemical shifts also differs. The isotope shift data can be accommodated if both **1** and **2** have similarly flat potential

energy surfaces for the bending motion associated with bridging. The large intrinsic isotope shifts should be regarded as being diagnostic for the existence of the low-energy bending motion where the shielding is significantly dependent on the degree of bending. Thus the isotope effects are not directly reflective of the extent of bridging in a three-center, two-electron bond but rather the mutability of a three-center, two-electron bond. On the other hand, the carbon chemical shifts which depend upon both the electron density and the carbon hybridization may be more diagnostic for the degree of bridging in the vibrationally averaged structure. The temperature dependence of the chemical shifts may be useful in further defining the shape of the potential energy surface.

A relatively flat potential energy surface for atomic motion is likely to be associated with three-center, two-electron bonding, i.e., nonclassical σ-delocalized bonding.³¹ Isotope shifts have been useful as a diagnostic tool for the existence of such bonding, for instance in distinguishing bonding in a mercurinium ion from bonding in a bromonium ion.¹¹ On the basis of our comparison of **1** and **2**, we believe that it is the shallow potential energy surface (and associated changes in shielding over that surface) that is ultimately responsible for the unusually large intrinsic NMR isotope shifts found for nonclassically bonded structures.⁶ Since the flat surface may occur even when bridging is not very extensive, the isotope shift may be a particularly sensitive probe for such bonding.

If a nonclassically bonded structure could have narrow potential wells for any motions leading to shielding changes, only small isotope shifts would be expected. In this regard, interesting systems for further investigation are two μ-hydrido-bridged ions: 1,6-dimethylcyclooctyl-d₃ cation (**14**) and 1,5-dimethylcyclooctyl-d₃ cation (**15**). Sorensen has reported a small isotope shift (0.6 ppm between C₁ and C₆) for **14**³² and large, temperature-dependent isotope shifts (1.4–2.7 ppm between C₁ and C₅) for **15**.³³ This difference could signify different shapes of the potential well for motion of the bridging atom; Sorensen has noted that the cyclooctyl cations have a very shallow surface for the bridging motion.²⁴

Experimental Section

NMR Spectroscopy. ¹³C NMR spectra of cations were acquired at 68.9 MHz with an IBM Model WP-270 SY NMR spectrometer or at 75.4 MHz with a Varian Model XL-300 spectrometer. The spectra were acquired within 1000 scans by using a 30–60° pulse, 2.0–4.5-s repetition rate, 64K data points, and 15 000–25 000-Hz spectral width. Spectra were run unlocked and chemical shifts were referenced to internal CH₂Cl₂ (53.62 ppm) on the Varian instrument or with a concentric 5-mm insert containing acetone-d₆ for lock and Me₄Si as reference for spectra run on the IBM instrument. The reported temperatures for the measurements on the Varian instrument were read directly from the calibrated (CH₃OH) thermocouple monitor and varied less than 1 °C during each acquisition. The spectrum of 2-norbornanone was obtained on a Bruker WM-500 spectrometer at 125.8 MHz.

Cation Preparation. The general procedure was to add in small portions ca. 2 mmol of the appropriate cation precursor to a cooled, vortex-stirred solution of ca. 10 mmol of 1:1 FSO₃H/SbF₅ in SO₂ClF (2.0 mL). The cation solution was then transferred by precooled pipet to a precooled 10-mm NMR tube. Variations involved the type of precursor (chloride or alcohol), solvent used for transfer of the precursor, and the temperature (ion, precursor type, transfer solvent, temperature): **1**, Cl, SO₂ClF, -130 °C; **2**, OH, CH₂Cl₂, -78 °C; **4**, Cl, none, -78 °C; and **5**, OH, SO₂ClF, -78 °C. The ratio of isotopomers was usually 2:1 labeled to unlabeled, although this ratio was varied in some repeat measurements. Cation **2b** was prepared from the chloride by using SbF₅ in SO₂ClF as described in the Results section.

Cation Precursors. The following alcohols were synthesized in 60–95% yield in standard Grignard reactions in ether with either methylmagnesium iodide or (methyl-d₃)magnesium iodide and the appropriate ketone: 2-methyl-2-bicyclo[2.2.2]octanol and its methyl-d₃, 3,3-d₂, and

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6-*d* isotopomers; 2-methyl-*endo*-2-bicyclo[2.2.1]heptanol and its methyl-*d*₃ and 3,3-*d*₂ isotopomers; 2-cyclopropyl-2-propanol and the 1,1,1,3,3,3-*d*₆ isotopomer; and 2-methyl-2-adamantanol and the methyl-*d*₃ isotopomer. Alcohols were purified by dry column flash chromatography using Merck silica gel 60 (finer than 230 mesh) or preparative gas chromatography on a 6-m column packed with 5% Carbowax on 80/100 mesh Chromosorb W High Pack. Chlorides were prepared by the procedure of Brown et al.³⁴ or the procedure of Norris and Olmstead³⁵ and were used without further purification.

Bicyclo[2.2.2]octan-2-one-3,3-*d*₂ and bicyclo[2.2.1]heptan-2-one-3,3-*d*₂ were prepared as previously described.³⁶ Cyclopropyl methyl-*d*₃ ketone was obtained by three repetitions of base-catalyzed (K₂CO₃) exchanges of cyclopropyl methyl ketone in D₂O as 55–60 °C for 15 h.

Bicyclo[2.2.2]octan-2-one-6-*d* was prepared by the sequence shown in Scheme I. The Diels–Alder reaction³⁷ of 2-((trimethylsilyloxy)-1,3-cyclohexadiene³⁶ with acrylonitrile in toluene at 140 °C for 48 h afforded

2-cyano-5-((trimethylsilyloxy)-5-bicyclo[2.2.2]octene in 92% yield. Methanolysis of the silyl enol ether with CH₃OD catalyzed by NaOCH₃ gave 5-cyanobicyclo[2.2.2]octan-2-one-2,2-*d*₂ in 78% yield. Conversion to the tosylhydrazone in ethanol (substantial loss of deuterium occurred here) and reduction³⁸ gave 2-cyanobicyclo[2.2.2]octane-6-*d* in 66% yield. Conversion to bicyclo[2.2.2]octan-2-one-6-*d* was accomplished by chlorination and hydrolysis in the method of Freeman et al.³⁷

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Registry No. 1, 66344-74-9; 2, 3197-78-2; 4, 27411-03-6; 5, 25681-56-5; D₂, 7782-39-0; bicyclo[2.2.2]octan-2-one-6-*d*, 110773-20-1; 2-cyano-5-((trimethylsilyloxy)-5-bicyclo[2.2.2]octene, 110773-21-2; 5-cyanobicyclo[2.2.2]octan-2-one-3,3-*d*₂, 110773-22-3; 2-cyanobicyclo[2.2.2]octane-6-*d*, 110773-23-4; 2-((trimethylsilyloxy)-1,3-cyclohexadiene, 54781-19-0; 2-methyl-6-deuteriobicyclo[2.2.2]octan-2-ol, 110773-24-5; 2-chloro-6-deuterio-2-methylbicyclo[2.2.2]octane, 110773-25-6.

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Self-Diffusion Coefficients of Solvents in Polystyrene Gels

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Abstract: Self-diffusion coefficients of toluene, acetonitrile, chloroform, and dichloromethane in swollen 1–20% cross-linked polystyrene beads have been determined by application of a new model to magnetization-transfer ¹³C NMR data for exchange of solvent in and out of the beads. The results agree closely with solvent self-diffusion coefficients in the same samples determined independently by the pulsed-gradient spin-echo NMR method. The new method also has been applied to self-diffusion of dichloromethane in macroporous polystyrene beads.

Self-diffusion coefficients of constituents of polymer solutions, plasticized polymers, micelles, microemulsions, and lyotropic and smectic liquid crystals have been determined by the pulsed-gradient spin-echo (PGSE) NMR method.^{1–7} We report here a new method for determination of self-diffusion coefficients of solvents in polystyrene beads and in the pores of macroporous polystyrenes based on magnetization-transfer NMR (MT-NMR), and the application of the PGSE method to the same samples. Previously PGSE NMR experiments showed that the self-diffusion coefficients of toluene in cross-linked polystyrene beads were equal to those in toluene solutions of linear polystyrene containing the same weight fraction polymer as in the gel.⁸

The MT-NMR method is based on the observation that polystyrene beads packed into an NMR tube and swollen with solvent frequently show two peaks for each solvent carbon atom in their ¹³C NMR spectra.^{9–11} Those peaks can be assigned to solvent inside and outside the beads on the basis of the spin–lattice relaxation times (*T*₁) and on the basis of relative peak areas in spectra of samples that contain much more interstitial solvent than intraparticle solvent.⁹ The rate of exchange of solvent between the two environments is of the same order of magnitude as the rate of spin–lattice relaxation and can be followed by selective

inversion–recovery *T*₁ experiments. Nonlinear least-squares analysis of the data provides *T*₁'s of the solvent in each environment and a first-order rate constant for exchange. Separate resonances for solvents and ions inside and outside of polymer beads have been reported earlier in both ¹H^{12–19} and ¹³C^{9–11,20} NMR spectra.

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