The Structure of the 2-Bicyclo[2.1.1]hexyl Cations Based on Their ^1H and ^{13}C Nuclear Magnetic Resonance Spectroscopic Study[1]

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Abstract: A series of 2-bicyclo[2.1.1]hexyl cations have been prepared under stable ion conditions and studied by ^1H and ^{13}C NMR spectroscopy. NMR data indicate that the tertiary ions **2** and **3** are typical carbenium ions with limited σ delocalization. The degenerate equilibrations observed in both secondary **1** and tertiary **2** ions are best represented by exchanging carbocation systems in which carbenium ion intermediates are the major contributors for the averaged NMR shifts, although the equilibration obviously involves σ-bridged carbonium ions.

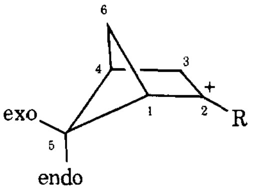
Introduction

The carbocationic intermediates of solvolysis (or deamination) of 2-bicyclo[2.1.1]hexyl derivatives have been of considerable interest.[2] Seybold, Vogel, Saunders, and Wiberg[3] recently reported the ^1H NMR spectrum of the long-lived 2-bicyclo[2.1.1]hexyl cation (**1**) and considered it to be an equilibrating σ-bridged ion in agreement with the solvolytic studies of Meinwald and Gassman.[4] The ^1H NMR spectrum of ion **1** in SbF_5-SO_2ClF solution showed three resonances at δ 8.32 (two protons), 3.70 (six protons), and 2.95 (one proton) with no line broadening observed in the temperature range studied (−90–−120 °C), indicating that the six methylene protons (H_3, H_5, and H_6) are equivalent on the NMR time scale.

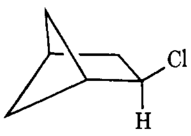
We have previously studied[5] the related 2-bicyclo[2.2.1]heptyl (norbornyl) cations, as well 2-alkyl (aryl) and 1,2-dialkyl- (aryl) substituted 2-norbornyl cations, showing that σ-p delocalization between the C(1)-C(6) bond and the empty C(2) p orbital decreased in importance going from the parent secondary 2-norbornyl cation to tertiary 2-alkyl (aryl) to 1,2-dialkyl (aryl) ions. Our studies provided examples of completely bridged nonclassical, partially bridged, as well static and equilibrating classical 2-norbornyl cations.[6] The interesting ^1H NMR spectrum of the parent 2-bicyclo[2.1.1]hexyl cation reported by Saunders and Wiberg prompts us to report our proton and carbon-13 NMR spectroscopic studies of the parent, as well the 2-methyl, 2-hydroxy, and 2-phenyl 2-bicyclo[2.1.1]hexyl cations and our conclusion concerning the nature of these ions.

Results and Discussion

The parent secondary ion **1** was prepared from 2-chlorobicyclo[2.1.1]hexane (**5**)[7] in SbF_5-SO_2ClF solution at −130 °C, and the tertiary ions **2** and **3** were prepared from their corresponding alcohols in FSO_3H-SO_2ClF solution at −130 and −78 °C, respectively. The proton NMR spectrum of **1** (Figure 1a) is essentially identical with that previously reported by Saunders and Wiberg.[3] Corresponding to the ^1H NMR spectrum, the carbon-13 NMR spectrum of ion **1** also shows three resonances at $\delta_{^{13}C}$ 157.8 (doublet, $J_{^{13}C-H}$ = 184.5 Hz), 49.1 (triplet, $J_{^{13}C-H}$ = 156.9 Hz), and 43.4 (doublet, $J_{^{13}C-H}$ = 164.6 Hz), which are assigned to C(1) and C(2); C(3), C(5), and C(6); and C(4), respectively, based on the proton coupled ^{13}C NMR spectrum (Figure 1c). Warming the solution of ion **1** above −90 °C slowly gave the cyclohexenyl cation.[3,8]



1, R = H
2, R = CH_3
3, R = C_6H_5
4, R = OH



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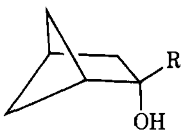
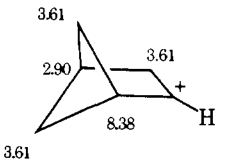


6, R = H
7, R = CH_3
8, R = C_6H_5

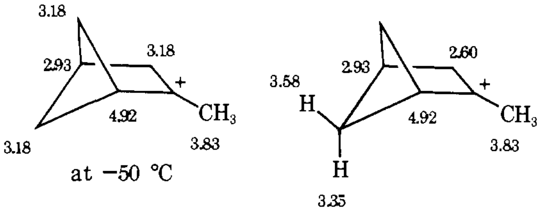
Although the ^1H NMR spectrum of ion **1** did not show reversible temperature-dependent behavior, it is evident, as shown in Figure 2, that the spectrum of the tertiary ion **2** is temperature dependent between −110 and −50 °C. No further changes in the ^1H NMR spectrum were observed above −50 °C until the ion slowly decomposed. As the temperature is raised from −110 to −50 °C, the two-proton signals at δ 2.60, 3.35, and 3.58 become equilibrated to give a six-proton signal centered at δ 3.18,[9] while the two one-proton doublets at δ 2.93 and 4.92 and the methyl singlet remain unchanged.

The singlets at δ 3.35 and 3.58 start to equilibrate (ca. −90 °C) before the signal at δ 2.60 shows appreciable broadening. The spectrum at −50 °C, thus, shows great similarity to that of the secondary ion **1** undergoing a similar degenerate process.



at −110 °C

1



at −50 °C

at −110 °C

2

In contrast, the 2-phenyl-2-bicyclo[2.1.1]hexyl cation (**3**) is found to be substantially stable up to 50 °C (sealed tube) in FSO_3H-SO_2ClF solution and does not show any temper-

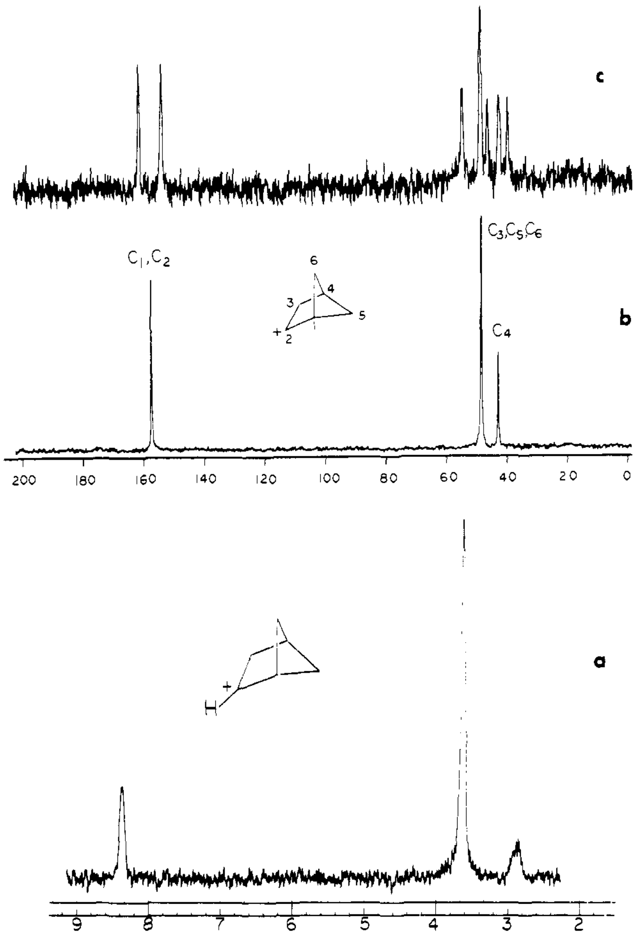


Figure 1. (a) ^{1}H NMR (60 MHz) spectrum of **1** in SbF_5-SO_2ClF solution at −110 °C; (b) proton noise-decoupled ^{13}C NMR spectrum of **1**; (c) proton coupled ^{13}C NMR spectrum of **1**.

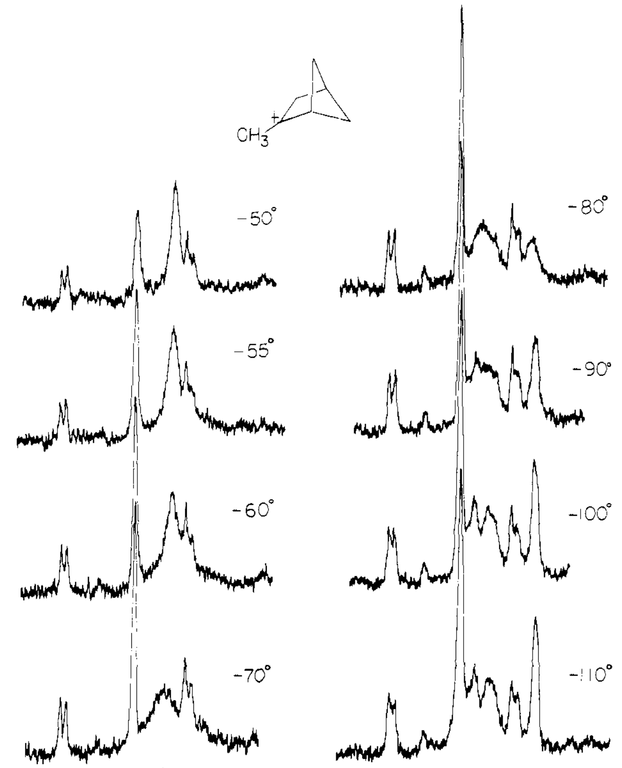


Figure 2. Temperature-dependent ^{1}H NMR spectra of **2**.

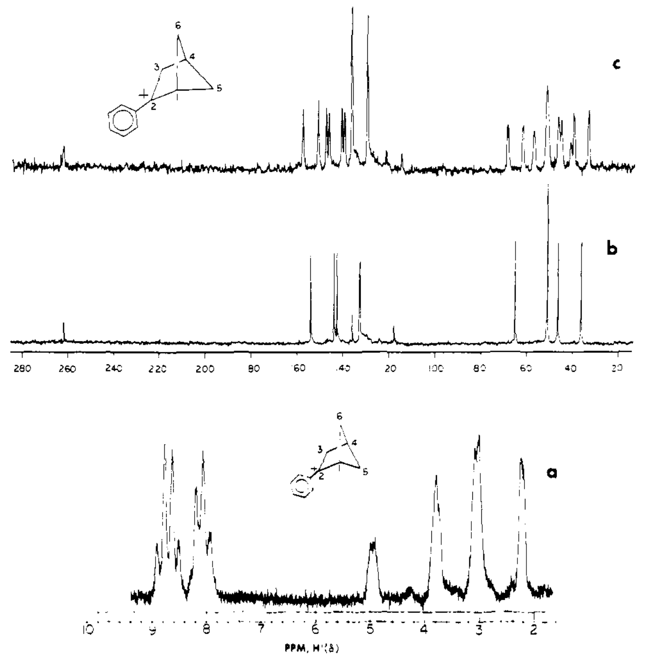


Figure 3. (a) ^{1}H NMR spectrum of **3** in FSO_3H-SO_2ClF solution; (b) proton noise-decoupled ^{13}C NMR spectrum of **3**; (c) proton coupled ^{13}C NMR spectrum of **3**.

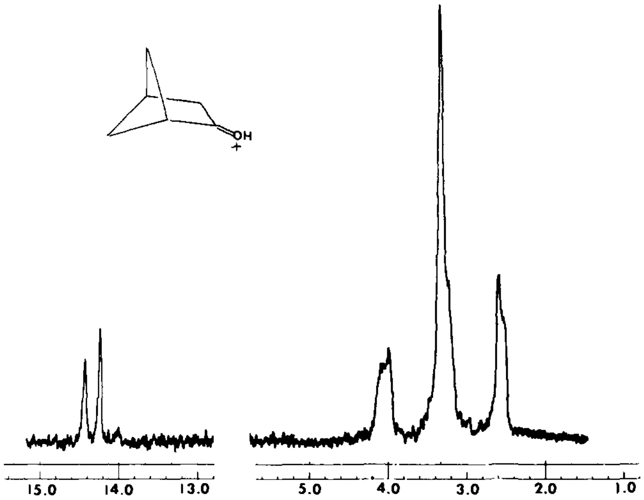
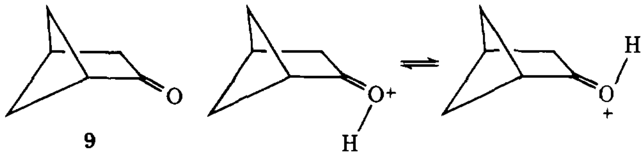


Figure 4. ^{1}H NMR spectrum (60 MHz) of **4** in FSO_3H-SbF_5-SO_2ClF solution at −60 °C.

ature dependence in its NMR spectrum (Figure 3), which is very similar to that of **2** obtained at −110 °C. The energy barrier for the degenerate equilibration process in **3** is apparently much higher than that in **2**, which in turn is higher than that in the parent ion **1**.

Protonation of bicyclic ketone **9**,[10] according to its ^{1}H NMR spectrum (Figure 4), produces two isomers as indicated by the two most deshielded absorptions at δ 14.22 and 14.42 (in a ratio of 1.5:1) at −60 °C. The two isomers of **4**



9

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do not equilibrate until the solution is warmed to ca. 15 °C. In FSO_3H-SO_2ClF solution, **9** gives essentially the same

Table I. ^{1}H and ^{13}C NMR Parameters of 2-Bicyclo[2.1.1]hexyl Cations[a]

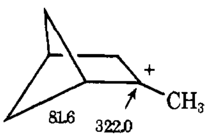
Ion	Temp, °C	1	2	3	4	5	6	Others
1	$\delta_{^1H}$ −110	8.38	8.38	3.61	2.90	3.61	3.61	
	$\delta_{^{13}C}$ −110	157.8	157.8	49.1	43.4	49.1	49.1	
		(d, 184.5)	(d, 184.5)	(t, 156.9)	(d, 164.6)	(t, 156.9)	(t, 156.9)	
2	$\delta_{^1H}$ −110	4.92		3.58	2.93	3.35 (exo)		3.83 (CH_3)
		(d, 4.2)		(m)	(d, 4.2)	2.60 (endo)		
	−50	4.92		3.18	2.93	3.18		
	$\delta_{^{13}C}$ −110	81.60	322.03	56.00	35.5	56.00	56.00	36.90 (CH_3)
		(d-d, 171.8, 10.6)	(s)	(t, 132.8)	(d-d, 165.0, 10.4)	(d-d, 156.0, 148.8)		(q, 130.0)
3	$\delta_{^1H}$ −60	4.95		3.82	3.00	3.08 (exo)		8.78 (ortho, d, 8.0); 8.12 (meta, d-d, 8.0, 6.0); 8.65 (para, t, 6.0)
		(d, 4.8)		(m)		2.24 (endo)		
	$\delta_{^{13}C}$ −60	65.0	261.3	46.3	36.2	50.9	50.9	C_{ortho}, 143.4 (d, 168.4), 142.1 (d, 168.5)
		(d-d, 164.4, 11.2)	(s)	(t, 134.7)	(d-d, 164.3, 10.8)	(d-d, 156.5, 145.8)		C_{meta}, 132.3 (d, 161.5), 132.1 (d, 161.5) C_{para}, 153.6 (d, 166.9) C_{ipso}, 135.4 (s)
4	$\delta_{^1H}$ −60	3.35		2.55	3.30	3.35		14.22 (OH) 14.42 (OH)
	$\delta_{^{13}C}$ −60	59.9	250.9	35.9	42.6	47.2	47.2	
		(d-d, 172.5, 5.6)	(s)	(t, 141.3)	(d-d, 162.0, 5.9)	(t, 145.6)	(t, 145.6)	

[a] ^{1}H and ^{13}C chemical shifts are in parts per million from external Me_4Si (capillary). Multiplicities and coupling constants (in Hz) are in parentheses; multiplicities: d = doublet, d-d = doublet of doublets, m = multiplet, q = quartet, s = singlet, t = triplet.

^{1}H NMR spectrum at −60 °C as that obtained in FSO_3H-SbF_5-SO_2ClF solution, except the absence of signal due to $=^+OH$ which should experience fast exchange with the solvent (FSO_3H). In FSO_3H-SbF_5-SO_2ClF solution, the exchange rate is appreciably much slower.

The structures of the 2-bicyclo[2.1.1]hexyl cations studied were further confirmed by the observation of long-range coupling between H_1 and H_4 in the ^{1}H NMR spectra and between C(1) and H_4, and C(4) and H_1 in the ^{13}C NMR spectra. The relevant coupling constants in the ^{1}H and ^{13}C NMR spectra of **2** and **3** are summarized in Table I.

The bridgehead carbon atom [C(1)] and the carbocationic center [C(2)] in **2** are about 15 and 60 ppm, respectively, more deshielded than the corresponding carbons in **3**. However, when **2** and the 2-methyl-2-norbornyl cation (**10**), as well as **3** and the 2-phenyl-2-norbornyl cation (**11**), are compared, one immediately notices that the electron-deficient center [C(2)] in **2** is about 50 ppm deshielded from that in **10**, while only a very small difference (~4 ppm) is found between **3** and **11**. Bridgehead carbon shifts in the two series of ions are comparable. The great difference in the C(2) carbon shifts between **2** and **10** cannot be the result of change in angle strain since only minimal change is observed going from **3** to **11**. In addition, the 2-methyl-2-bicyclo[2.1.1]hexyl cation **2** seems to show the characteristics of a classical carbenium ion, such as the 1-methyl-1-cyclopentyl cation (**12**), since they both show very similar deshielded carbon shifts for the carbocationic centers. These data seem to indicate that C–C σ-electron delocalization toward the empty p orbital in **2** is much more limited than in **10**, an ion we have previously concluded a partially σ delocalized ion.[5] This also is supported by the observation of very similar carbon shifts in the phenyl-substituted ions in both series, **3** and **11**, as they are compared with the 1-phenyl-1-cyclopentyl cation (**13**), a phenylcarbenium ion with no significant σ delocalization. The carbon-shift difference at the cationic center between **12** and **13** (57.8 ppm) is, thus, very close to that found between **2** and **3** (60.7 ppm), while the difference between **10** and **11** is much smaller (13.8 ppm!).



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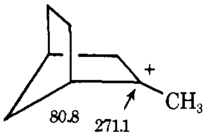

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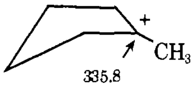

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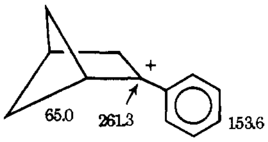

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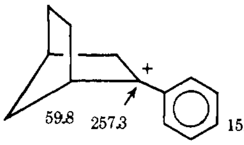

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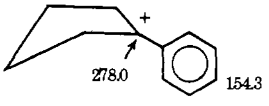

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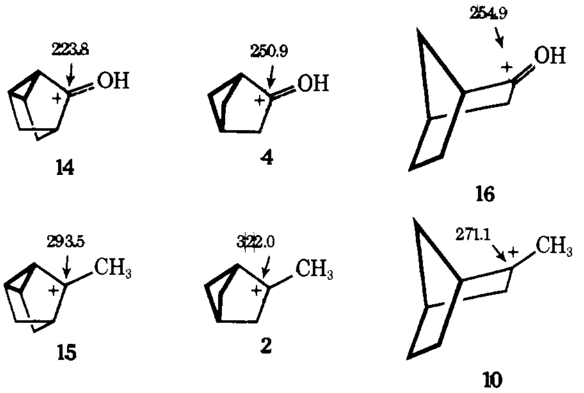
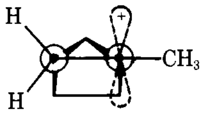
The ineffectiveness of a cyclobutyl relative to a cyclopropyl ring in stabilizing a neighboring electron-deficient center is known.[11] It is, thus, interesting to compare the effect of cyclopropyl, cyclobutyl, and cyclopentyl rings toward delocalizing charge at a neighboring carbocation center in bicyclic or tricyclic carbocations. We have obtained the ^{13}C NMR spectrum of the protonated 2-bicyclo[2.1.1]hexanone (**4**) in FSO_3H-SO_2ClF solution and have summarized ^{13}C NMR parameters in Table I. For comparison, we have shown the carbon shifts of carbocationic center in the 3-nortricyclyl (**14** and **15**),[12] 2-bicyclo[2.1.1]hexyl (**4** and **2**), and 2-bicyclo[2.2.1]heptyl (**16** and **10**)[5c] cations, wherein cyclopropyl, cyclobutyl, and cyclopentyl rings are incorporated, respectively. **4** and **16** show comparable carbon shifts, while that in **14** is significantly shielded due to charge delocalization into the cyclopropyl ring. The carbon-shift difference between **4** and **14** (27.1 ppm) is similar to that between **2** and **15** (28.5 ppm). Apparently, the cyclopropyl

Scheme I



ring is much more effective at delocalizing positive charge than the cyclobutyl ring. Furthermore, carbon-shift differences between **4** and **2** (71.1 ppm) and between **14** and **15** (69.7 ppm) are comparable. The difference between **16** and **10** (16.2 ppm) is, however, much smaller. Again, this shows that the 2-methyl-2-norbornyl cation (**10**), indeed, should be treated as a partially σ-delocalized ion as previously described.[5]

The present NMR spectroscopic study shows the significant difference between the tertiary 2-methyl-2-bicyclo[2.1.1]hexyl and 2-methyl-2-bicyclo[2.2.1]heptyl cations. Charge delocalization through carbon–carbon bond is much less significant in **2** than in **10**. Models show that the neighboring carbon–carbon bond in **10** is oriented much more favorably to interact with the carbocationic empty p orbital than that in **2**. Although we were not able to freeze out, on the NMR time scale, the equilibration of the parent 2-bicyclo[2.1.1]hexyl cation **1**, the parent 2-bicyclo[2.2.1]heptyl (2-norbornyl) cation **17** could be frozen out at −150 °C as the static nonclassical, bridged carbonium ion.[5,6] It is obvious that the degenerate equilibrating process observed in **1** (and in any Wagner–Meerwein type rearrangement) also go through σ-bridged carbonium ion, such as **18**. In more strained systems as the bicyclo[2.1.1]hexyl system, the bridged carbonium ions could become energetically less favorable and, therefore, may not contribute significantly to the observed NMR parameters.



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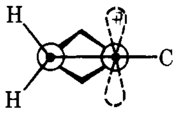

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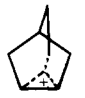

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18

Experimental Section

Materials. The 2-bicyclo[2.1.1]hexanone (**9**), 2-bicyclo[2.1.1]hexanol (**6**), and 2-chlorobicyclo[2.1.1]hexane (**5**) were prepared as previously described.[4,7]

2-Methyl- and 2-phenyl-2-bicyclo[2.1.1]hexanols were prepared from **9** by reaction with methyl and phenyl Grignard reagents, respectively: **7**, mp 8–9 °C; **8**, mp 36–38 °C.

Preparation of Ions. A freshly prepared FSO_3H-SO_2ClF (or SbF_5-SO_2ClF) solution was cooled to dry ice-ethanol bath temperature (ca. −130 °C). To the acid solution was then slowly added with vigorous stirring a cold solution of appropriate chloride or alcohol in SO_2ClF to give an approximately 15% solution of the ion. The ion solution was then immediately transferred into a precooled NMR tube for study.

Proton and Carbon-13 NMR Spectroscopy. ^{1}H NMR spectra were obtained using Varian Associates Model A56/60A NMR spectrometer, equipped with a variable-temperature probe. Me_4Si (capillary) was used as reference. ^{13}C NMR spectra were obtained using a Varian VFT XL-100-15 spectrometer equipped with a broad-band proton noise decoupler and a variable-temperature probe. The instrument was operated in the pulse Fourier transform mode. Carbon shifts were measured from the ^{13}C signal of capillary tetramethylsilane (5% enriched).

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