Structural Effects in Solvolytic Reactions. 36. Effect of Increasing Electron Demand on Carbon-13 Nuclear Magnetic Resonance Shifts in the 1-Aryl-1-cyclohexyl and 1-Aryl-1-cycloheptyl Carbocations. Further Test of the Ability of the σ^{C^+} Constants to Correlate Carbon-13 Nuclear Magnetic Resonance Shifts

Herbert C. Brown* and Mariappan Periasamy

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

The ^{13}C NMR shifts of a series of meta- and para-substituted 1-phenyl-1-cyclohexyl and 1-phenyl-1-cycloheptyl carbocations were measured in $SbF_5/FSO_3H/SO_2ClF$ at $-80\ °C$ to provide a further test of the ability of the new set of σ^{C^+} constants to correlate such ^{13}C NMR shifts. Indeed, the data reveal excellent linear correlation of the observed shifts, $\Delta\delta^{C^+}$, in these two systems by the σ^{C^+} constants. The 1-aryl-1-cyclohexyl system yields a ρ^{C^+} value of -17.2, with a correlation coefficient of $r = 0.999$. The 1-aryl-1-cycloheptyl system gives $\rho^{C^+} = -16.4$, with $r = 0.999$. Previous investigation of the 1-aryl-1-cyclopentyl system yielded $\rho^{C^+} = -16.8$, with $r = 0.999$. Thus all of the systems containing five-, six-, and seven-membered rings are correlated with satisfactory precision by the σ^{C^+} values. The variation in ρ^{C^+} from the five-, to the six-, to the seven-membered systems parallels the changes in ρ^+ observed in solvolysis of the p-nitrobenzoates. However, the variations with ring size are larger in the solvolytic studies. It is concluded that both ground-state energies and the electronic stabilization of the cations are enhanced in the five- and seven-membered rings, contributing to the change in ρ^+ from that observed for the six-membered ring. On the other hand, differences in ground-state energies can play no role in the magnitude of ρ^{C^+} for the fully formed carbocations.

We recently proposed a new set of substituent constants, σ^{C^+}, to correlate ^{13}C NMR shifts in tertiary aryldialkyl carbocations.[1] We are presently engaged in testing the ability of these substituent constants to correlate ^{13}C NMR shifts in representative systems.

In the original study we established that the data for 1-aryl-1-cyclopentyl carbocations (1) are nicely correlated by σ^{C^+} values.[1] In a recent publication, we tested 2-aryl-2-butyl and 4-aryl-4-heptyl carbocations and found that both systems are nicely correlated[2] (Figure 1).

In a related study, Kelly and co-workers tested the 3-aryl-3-pentyl and 2-aryl-2-adamantyl systems.[3] Recently, Farnum and Clausen also reported data for several 2-aryl-2-adamantyl derivatives.[4] In both systems, the data exhibit excellent correlations with the σ^{C^+} constants.

It appeared desirable to examine the effect of ring size on such correlation of $\Delta\delta^{C^+}$ shifts with σ^{C^+} values. Accordingly, we decided to examine the 1-aryl-1-cyclohexyl and 1-aryl-1-cycloheptyl systems (2 and 3).

1   2   3
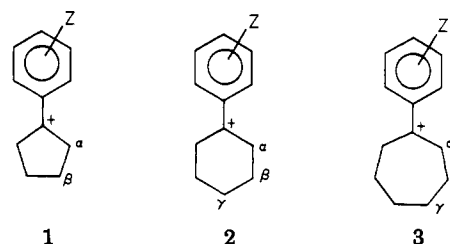
In addition to providing a further test of the range of applicability of the new σ^{C^+} constants, the data, together with the earlier results on the 1-aryl-1-cyclopentyl system (1), would permit a comparison of the effects of ring size on the variation in ρ^+ observed in solvolysis[5] with the variation in ρ^{C^+} observed for ^{13}C shifts of the cationic centers in the carbocations.

Results and Discussion

The 1-aryl-1-cyclohexanols (4) and 1-aryl-1-cycloheptanols (5) were synthesized by the addition of the

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(3) Kelly, D. P.; Jenkins, M. J.; Mantello, R. A. *J. Org. Chem.* 1981, 46, 1650.

(4) Farnum, D. G.; Clausen, T. P. *Tetrahedron Lett.* 1981, 549.

(5) Brown, H. C.; Ravindranathan, M.; Peters, E. N.; Gundu Rao, C.; Rho, M. M. *J. Am. Chem. Soc.* 1977, 99, 5373.

Table I. ^{13}C NMR Shifts[a] of 1-Aryl-1-cyclohexyl Carbocations 2 in SbF$_5$/FSO$_3$H/SO$_2$ClF at -80 °C

substituent (Z)	chemical shift										
	C$^+$	C$_\alpha$	C$_\beta$	C$_\gamma$	C$_Z$	C$_1$	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$
p-OCH$_3$	226.8	39.7	35.4	26.9	59.7	131.5	144.5	120.1	183.1	120.1	144.5
p-CH$_3$	250.8	43.4	39.5	27.3	24.9	136.2	140.7	134.5	174.5	134.5	140.7
p-F	255.3	44.7	40.6	27.2		135.2	145.7	121.7	181.0	121.7	145.7
	(4.3)						(16.5)	(22.1)	(292.3)	(22.1)	(16.5)
p-Cl	258.8	45.4	41.7	27.5		136.6	141.3	134.0	165.5	134.0	141.3
m-CH$_3$	260.3	45.2	41.5	27.4	20.8	138.3	138.3[b]	144.6	157.0	133.1	140.2[b]
H	262.5	45.5	41.7	27.4		138.3	140.5	133.3	155.5	133.3	140.5
m-F	268.4	47.6	44.2	27.7		139.5	124.2	164.7	141.6	137.2	135.0
						(7.7)	(22.3)	(254.8)	(22.4)		(7.0)
m-Cl	268.5	47.5	44.4	27.8		139.6	139.4[b]	138.1	153.4	134.4	138.8[b]
m-CF$_3$[c]	271.8	48.3	45.2	27.9							
3,5-Cl$_2$	273.7	49.4	47.0	28.0		139.7	140.1	136.4	150.9	136.4	140.1
p-CF$_3$[c]	275.3	49.4	46.7	27.9							
3,5-(CF$_3$)$_2$[c]	278.9	51.0	48.9	28.3							

[a] In parts per million downfield from Me$_4$Si (capillary). Assignments for aliphatic carbon signals are based on comparison with previously reported assignments for the 1-phenyl-1-cyclohexyl cation.[7] The aromatic carbon signals are assigned by comparison with the previously reported values for other systems.[1,2] ^{13}C-F coupling constants (in hertz) are in parentheses. [b] Assignments may be interchanged. [c] The ions slowly decompose in the probe (new, small peaks start appearing). The CF$_3$ and some of the aromatic carbon signals are comparatively weak and were not assigned.
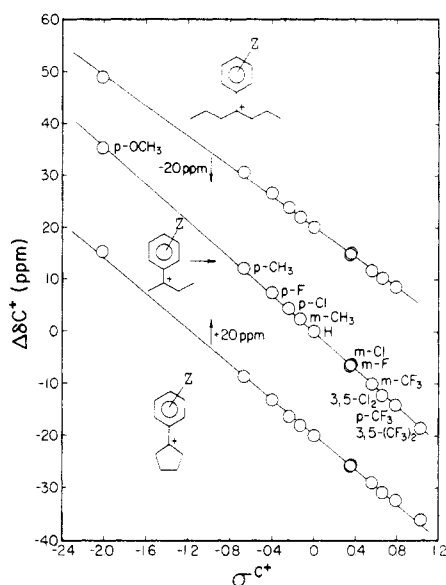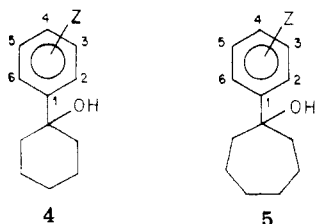

Figure 1. $\Delta\delta^{C^+}$-σ^{C^+} plots for 4-aryl-4-heptyl, 2-aryl-2-butyl, and 1-aryl-1-cyclopentyl carbocations.

corresponding ketone to the Grignard reagents prepared from the corresponding substituted bromo- or iodobenzenes.

4   5

The "magic acid" reagent was prepared by mixing equimolar amounts of SbF$_5$ and FSO$_3$H. This material was dissolved in sufficient SO$_2$ClF to give a solution that is ~3 M in these two components. The carbocations were prepared by adding a measured quantity of the alcohol to the above solution at -78 °C to give a solution that is approximately 0.5 M in the carbocation. The ^{13}C shifts were then measured at -80 °C.

1-Aryl-1-cyclohexyl System. Several 1-aryl-1-cyclohexyl carbocations were previously studied by Farnum and co-workers[6] [p-OCH$_3$, 3,4-(CH$_3$)$_2$, p-CH$_3$, p-F, p-Cl, p-Br,
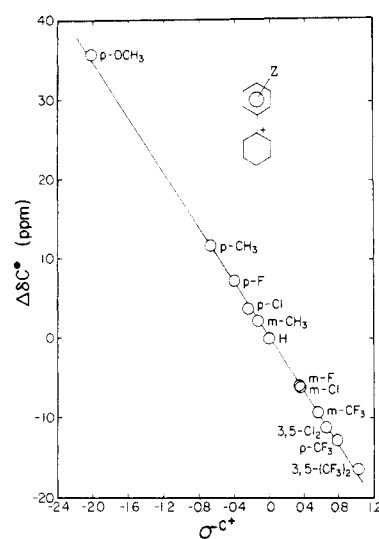

Figure 2. Plot of $\Delta\delta^{C^+}$ against σ^{C^+} values for 1-aryl-1-cyclohexyl cations: correlation coefficient, r = 0.999; slope, ρ^{C^+} = -17.17; standard deviation, SD (ρ^{C^+}) = 0.18; standard deviation, SD ($\Delta\delta^{C^+}$) = 0.46.

H, m-F, p-CF$_3$, 3,5-(CF$_3$)$_2$]. Unfortunately, they used two different solvents but did not report which solvent was used for each cation. Moreover, they report data only for the C$^+$ shifts. In view of our need for chemical shift data under rigorously controlled conditions, we decided to run our entire series of 12 compounds under identical experimental conditions.

The data are summarized in Table I. An excellent fit is realized for the observed shifts, $\Delta\delta^{C^+}$, against the σ^{C^+} constants (Figure 2). The correlation yields a ρ^{C^+} value of -17.2, with a correlation coefficient of r = 0.999.

1-Aryl-1-cycloheptyl System. The 1-phenyl-1-cycloheptyl carbocation was previously prepared and examined by Olah and Liang.[7] Unfortunately, the authors did not specify the precise conditions of solvent, temperature, and concentration. Accordingly, we undertook to prepare and examine our entire series of 12 derivatives under our defined, standardized, experimental conditions. Unfortu-

(6) Farnum, D. G.; Botto, R. E.; Chambers, W. R.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847.

(7) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 195.

(8) Kirchen, R. P.; Okazawa, N.; Ranganayakulu, K.; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 597.

Table II. ^{13}C NMR Shifts^a of 1-Aryl-1-cycloheptyl Carbocations 3 in SbF$_5$/FSO$_3$H/SO$_2$ClF at -80 °C

substituent (Z)	chemical shift										
	C$^+$	C$_\alpha$	C$_\beta$	C$_\gamma$	C$_Z$	C$_1$	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$
p-OCH$_3$	228.9	40.1	28.7	27.6	59.5	133.3	144.7	119.6	181.7	119.6	144.7
p-CH$_3$	252.5	43.7	29.0	27.7	24.8	137.7	140.8	134.2	173.0	134.2	140.8
p-F	256.7 (4.5)	45.0	29.0	27.6		136.7	145.8 (16.1)	121.5 (22.2)	179.8 (291)	121.5 (22.2)	145.8 (16.1)
p-Cl	259.8	45.5	29.0	27.5		137.9	141.3	133.6	163.8	133.6	141.3
m-CH$_3$	261.5	45.4	29.0	27.8, 27.4	20.8	140.0	140.2^b	144.2	155.5	132.8	138.3^b
H^c	263.6	45.8	28.9	27.5		139.7	140.5	133.0	154.2	133.0	140.5
m-F	268.7	47.7 47.5	29.0 28.7	27.8 27.2		141.2	124.2 (21.9)	164.3 (254.2)	140.3 (22.0)	137.1	134.6 (7.5)
m-Cl	268.8	47.6	28.9	27.6 27.4		138.1	140.7^b	138.7	152.1	134.0	139.3^b
m-CF$_3$^{d}	271.8	48.4	28.9	27.4							
3,5-Cl$_2$	273.1	49.2	28.8	27.5		139.8	141.0	136.5	149.8	136.5	141.0
p-CF$_3$^{d}	275.1	49.4	28.8	27.4							

^{a} In parts per million downfield from Me$_4$Si (capillary). Assignments of aliphatic carbon signals are based on previously reported assignments for the 1-phenyl-1-cycloheptyl carbocation.[7] The aromatic carbon signals are assigned by comparison with the previously reported values for other systems.[1,2] ^{13}C–F coupling constants (in hertz) are in parentheses. Attempt to prepare the 3,5-(CF$_3$)$_2$ ion were unsuccessful. ^{b} Assignments may be interchanged. ^{c} Recently, Sorensen and co-workers assigned the peak at 27.5 ppm for the C$_\beta$ carbon and the peak at 28.9 ppm for the C$_\gamma$ carbon atom.[8] Accordingly, the assignments for the C$_\beta$ and C$_\gamma$ carbon atoms in these 1-aryl-1-cycloheptyl cations are not certain. ^{d} The ions decompose in the probe (i.e., new, small peaks start appearing). The CF$_3$ and some of the aromatic carbon signals are comparatively weak and were not assigned.
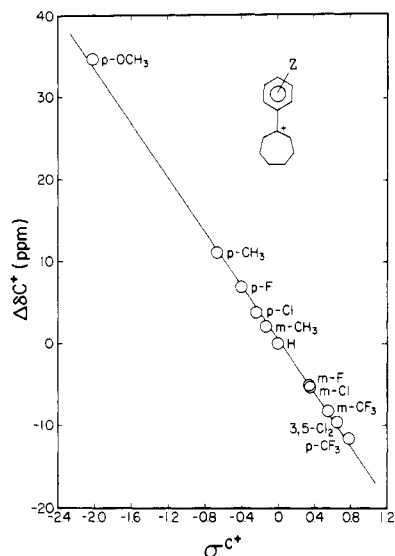

Figure 3. Plot of $\Delta\delta^{C^+}$ against σ^{C^+} values for 1-aryl-1-cycloheptyl cations: correlation coefficient, $r = 0.999$; slope, $\rho^{C^+} = -16.37$; standard deviation, SD $(\rho^{C^+}) = 0.26$; standard deviation, SD $(\Delta\delta^{C^+}) = 0.60$.

nately, it proved impossible to prepare the carbocation from the last member of the series, 3,5-(CF$_3$)$_2$, for observation. The cation apparently forms but rapidly undergoes chemical change to other unidentified species.

The data for the other 11 members are summarized in Table II. Here also a plot of the ^{13}C shifts, $\Delta\delta^{C^+}$, against the σ^{C^+} values, reveals an excellent correlation (Figure 3). The correlation yields a ρ^{C^+} value of -16.4, with a correlation coefficient of 0.999.

Comparison of the Effect of Ring Size in Solvolysis and in Cationic Carbon Chemical Shifts. It has long been recognized that ring size can have major effects on chemical reactivity.[9] It has been of major interest that such changes in chemical reactivity with ring size exhibit a consistent pattern.[9] Such patterns have been utilized to explore the factors influencing chemical behavior.[10,11]

The high reactivities exhibited by the solvolysis of secondary[10] and tertiary[12] cyclopentyl derivatives have been attributed to bond opposition forces.

It was proposed that the ionization of the chloride from the five- (6) and seven-membered ring (8) is greatly facilitated by bond opposition forces, a factor absent in the corresponding solvolysis of 1-methyl-1-cyclohexyl chloride (7).

rel rate (25 °C)   **6** 124.0   **7** 1.00   **8** 108.0
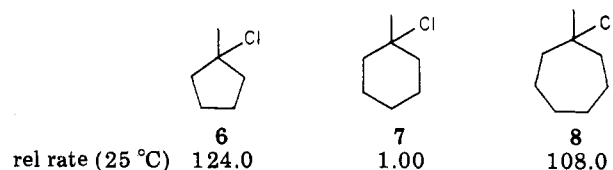
Similar differences in reactivities are observed in the solvolysis of the corresponding p-nitrobenzoates of 1-phenyl-1-cycloalkanols[5] (9–11). The differences in reactivity are attributed to the same factor.

rel rate (25 °C)   **9** 178.0   **10** 1.00   **11** 51.5
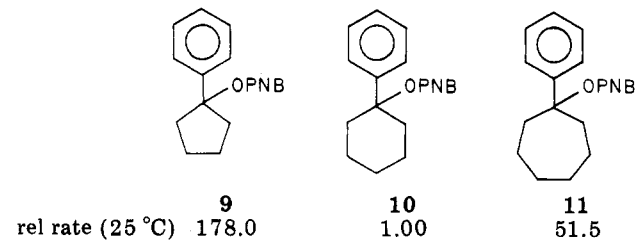
Examination of the effect of such cycloalkyl groups in the para position of the *tert*-cumyl system revealed similar effects, although much smaller.[13,14]

Unfortunately, solvolytic rate data is not available for p-cycloheptyl-*tert*-cumyl chloride. However, benzoylation data are available for all three systems[15] (14–16). They reveal the same pattern of reactivity.
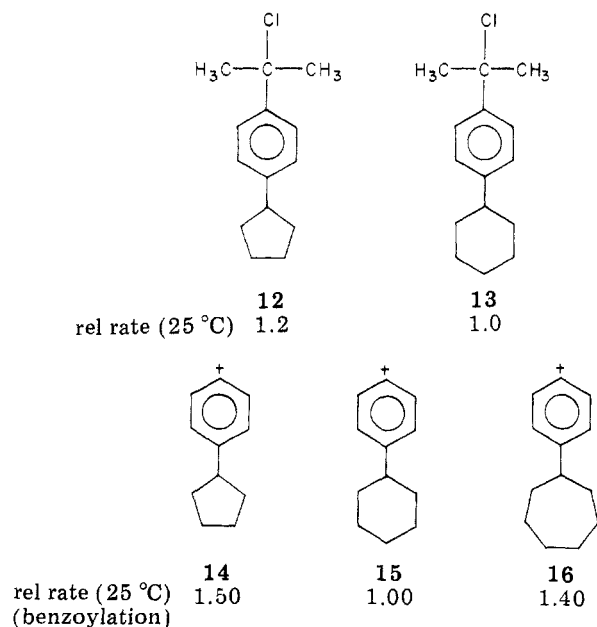
(9) Prelog, V. *J. Chem. Soc.* **1950**, 420.
(10) Brown, H. C.; Ham, G. *J. Am. Chem. Soc.* **1956**, 78, 2735.

(11) Brown, H. C.; Ichikawa, K. *Tetrahedron* **1957**, 1, 221.
(12) Brown, H. C.; Borkowski, M. *J. Am. Chem. Soc.* **1952**, 74, 1894.
(13) Hahn, R. C.; Corbin, T. F.; Shechter, H. *J. Am. Chem. Soc.* **1968**, 90, 3404.
(14) Brown, H. C.; Gnedin, B. G.; Takeuchi, K.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, 97, 610. Other groups such as p-cyclobutyl and exo- and endo-norbornyl reveal a similar pattern of reactivity.
(15) Smart, B. Ph. D. Thesis, University of California at Berkeley, 1970.

12
rel rate (25 °C) 1.2

13
1.0

14   15   16
rel rate (25 °C) 1.50   1.00   1.40
(benzoylation)

Table III. Variations in ρ Values

system	$\rho^{+\ a}$	ρ^{C^+}
1-aryl-1-cyclopentyl	−3.82 (17)	−16.8 ± 0.2[b] (1)
1-aryl-1-cyclohexyl	−4.60 (18)	−17.2 ± 0.2[c] (2)
1-aryl-1-cycloheptyl	−3.87 (19)	−16.4 ± 0.3[c] (3)

[a] Solvolysis of p-nitrobenzoates in 80% aqueous acetone.[5]   [b] Reference 1.   [c] Present study.

Table IV. Variations in ^{13}C NMR Shifts with Electron Demand

system	substituents compared	shift variation (downfield), ppm		
		$\Delta\delta C_\alpha$	$\Delta\delta C_\beta$	$\Delta\delta C_\gamma$
1-aryl-1-cyclopentyl (1)[a]	p-OCH$_3$ to p-CF$_3$	9.9	0.6	
1-aryl-1-cyclohexyl (2)[b]	p-OCH$_3$ to p-CF$_3$	9.7	11.3	1.0
1-aryl-1-cycloheptyl (3)[b]	p-OCH$_3$ to p-CF$_3$	9.3	0	0

[a] Reference 1.   [b] Present study.

Bond opposition forces should play no role in these reactions where no breaking or making of a bond involving the alicyclic ring occurs. The relative reactivities in these cases could be attributed to differences in hyperconjugation (C–C and C–H) contributions in these ring systems (Baker–Nathan-type effect).[16]

Although the developing positive charge is inside the ring in systems 6–11 and outside the ring systems 12–16, similar patterns of reactivity are observed. This suggests that in addition to the bond opposition forces influencing the relative reactivities of 6–11, hyperconjugation stabilization of the positive charge by the ring carbon orbitals may be more effective in the more strained five- and seven-membered rings than in the less strained six-membered ring.

Fortunately, the tool of increasing electron demand has been applied to the five-, six-, and seven-membered ring systems[5] (17–19). The same pattern of behavior is observed.

17   18   19
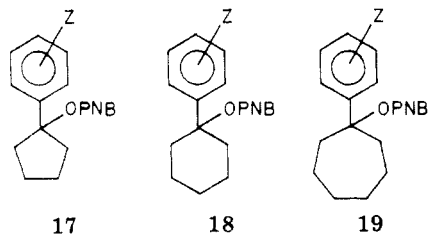
Consequently, we are now in a position to compare the effect of increasing electron demand on ρ^+ for such systems and to compare the results with those realized with increasing electron demand on the chemical shift for the cationic carbon in the carbocations.

The data for these sytems are summarized in Table III. We note that in solvolysis, ρ^+ changes from −3.82 for the 1-aryl-1-cyclopentyl system and −3.87 for the 1-aryl-1-cycloheptyl system to −4.60 for the 1-aryl-1-cyclohexyl system. This compares with changes in values of ρ^{C^+} from −16.8 for 1-aryl-1-cyclopentyl and −16.4 for 1-aryl-1-cycloheptyl to a value of −17.2 for 1-aryl-1-cyclohexyl. Therefore, the changes in ρ^{C^+} values with ring size are in the same direction as the corresponding changes in ρ^+.

values, with the value for the cyclohexyl system being the most negative in both cases. However, the variation in ρ^{C^+} with ring size is small compared to that observed in the solvolysis study. In the solvolytic studies, the changes in the ρ^+ values with ring size were attributed primarily to the operation of bond opposition forces,[5] with possible minor contributions by hyperconjugative and inductive contributions. On the other hand, the ^{13}C shift data involve no bond opposition forces. Consequently, the variations in the ρ^{C^+} values must be attributed to differences in the hyperconjugative and inductive contributions of the individual rings. This may explain the comparative insensitivity of the ρ^{C^+} values to the ring size.

Comparison of the Effect of Ring Size on ^{13}C Shifts of Other Carbons. Variations in C^α, C^β, and C^γ chemical shifts for 1-aryl-1-cyclohexyl and 1-aryl-1-cycloheptyl cations are summarized in Table IV along with those for 1-aryl-1-cyclopentyl carbocations.

Variations in α-carbon shifts for all three systems are of the same order of magnitude (Table IV). However, variation in the β-carbon shifts is somewhat unique for the cyclohexyl system. The β-carbon shift in the cyclohexyl system undergoes a downfield shift from p-OCH$_3$ to p-CF$_3$ of 11.3 ppm, compared to only 0.6 ppm for the cyclopentyl system. This difference in behavior may arise from differences in the ability of the C^β bonds to hyperconjugate through the C^β–C^α–C^+ chain, depending as it must on the dihedral angle of the C^β bonds and the C^β–C^α–C^+ plane.

In relatively planar rings like that of the cyclopentyl system, such hyperconjugative interaction of the C^β bonds with the electron-deficient center may not be significant, accounting for the very small change in the C^β shift with increasing electron demand in the 1-aryl-1-cyclopentyl cations.

Sorensen and Kirchen reported that the 1-methyl-1-cyclohexyl cation exists in a conformational equilibrium between the chain and twist–boat forms.[17] Our data of the C^β carbon atom in 1-aryl-1-cyclohexyl cations suggest that in these conformations the hyperconjugative interaction of the C^β bonds with the C^+ center may be more favorable.

Although the assignments of the chemical shifts for the C^β and C^γ carbon atoms in the 1-aryl-1-cycloheptyl cations are not certain,[7,8] it is evident from Table II that these

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(17) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* 1978, *100*, 1487.

Table V. Physical Constant Data[a] for 1-Aryl-1-cyclohexanols (4) and 1-Aryl-1-cycloheptanols (5)

substituent (Z)	alcohol 4		alcohol 5, mp or bp (mm), °C
	mp or bp (mm), °C	lit. mp, °C	
4-OCH$_3$	b		b
4-CH$_3$	56	55–77[c]	45
4-F	75	73–75[c]	32
4-Cl	79	77–79[c]	43
3-CH$_3$	80 (0.05)		29–30
H	67	66–67[c]	95 (0.1)[d]
3-F	56–57	52–54[c]	42
3-Cl	37		68
3-CF$_3$	63		66
3,5-Cl$_2$	48		98
4-CF$_3$	60	56–58[c]	90 (0.1)
3,5-(CF$_3$)$_2$	103	102–104[c]	64

[a] Satisfactory analytical data (+0.3% for C, H, Cl, and F) were obtained for all of the new compounds. [b] The alcohol dehydrates on distillation. The crude alcohol was used for preparation of the corresponding cation after satisfactory ^{13}C NMR spectral data were obtained. [c] Reference 6. [d] Lit.[20] bp 100 °C (0.5 mm).

shifts do not change with increasing electron demand at the C$^+$ center.

Sorensen and Kirchen also studied the 1-methyl-1-cycloheptyl cation.[17] They reported that this cation has low pseudorotational-type barriers among conformers of similar energy.[17] They also pointed out that their results are similar to the data reported for cycloheptanone.[18] Although the geometry of the stable conformation of cycloheptanone in solution is not clearly understood,[18] a twist–boat–chair conformation with the carbonyl group at one of the four different possible positions has been proposed to be lower in energy.[19] It is probable that the 1-aryl-1-cycloheptyl cations may also exist in such a twist–boat–chair conformation. Our results suggest that hyperconjugation of the C$^\beta$ bonds with the C$^+$ center may not be important in this conformation of 1-aryl-1-cycloheptyl cations.

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(19) Allinger, N. L.; Tribble, M. T.; Miller, M. A. *Tetrahedron* **1972**, *28*, 1173.
(20) Kahn, A. M.; McQuillin, F. J.; Jardine, I. *J. Chem. Soc. C* **1967**, 136.

Experimental Section

NMR Spectra. ^{13}C NMR spectra were recorded at –80 °C on a Varian CFT-20 spectrometer with 8-mm tubes containing a concentric 3-mm (o.d.) capillary tube of acetone-d_6 and Me$_4$Si,, 8192 data points, a spectral width of 6500 Hz, and a pulse angle of 45°. Chemical shifts are in parts per million downfield from external Me$_4$Si.

Precursors. 1-Aryl-1-cyclohexanols (4) and 1-aryl-1-cycloheptanols (5) were prepared by addition of the corresponding ketone to the Grignard reagent prepared from the corresponding substituted bromo- or iodobenzenes. The physical constant data for these precursors are summarized in Table V. All of the compounds gave ^{1}H NMR and ^{13}C NMR data in accordance with the assigned structures. Satisfactory elemental analyses were obtained for all of the new compounds.

Carbocations. The ions were prepared by slow addition of the appropriate precursor as a solution in SO$_2$ClF at –78 °C or as powder to a solution of FSO$_3$H/SbF$_5$ (1:1 M)/SO$_2$ClF cooled to –78 °C with rapid vortex mixing. The "magic acid", SbF$_5$/FSO$_3$H (1:1 M), concentration in the solution was 3 M. The concentration of the ion based on the alcohol added was ~0.5 M. Transfer of the solutions under nitrogen to an 8-mm NMR tube was achieved via a cooled double-ended syringe, as described previously.[21]

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