given in parts per million (ppm) downfield from anhydrous ^{15}NH$_3$ in δ units and coupling constants in cycles per second (Hz). ^{15}N Chemical shifts were obtained by using a 1:4 CH$_3{}^{15}$NO$_2$–CD$_2$Cl$_2$ solution as a secondary standard. Proton NMR data were obtained on a Varian EM-390 spectrometer. Chemical shifts are given in parts per million downfield from Me$_4$Si in δ units and coupling constants in cycles per second. For preparative vapor-phase chromatography (VPC), a Varian Aerograph Model 920 instrument equipped with a thermal conductivity detector and helium carrier gas was used. The VPC column was a 5 ft × 0.25 in. glass, Pennwalt 223 amine packing (Applied Sciences Laboratories, Inc.). All reactions were run under an argon atmosphere.

4-Oxa-2,2,6,6-tetramethylpiperidine-^{15}*N* (8). A 10.0 g (0.072 mol) sample of phorone **2** and ~100 mg of sodium hydroxide were placed in a 25-mL pyrolysis tube and then frozen under vacuum. An ammonia solution was prepared by neutralizing 5.0 g (0.092 mol) of ^{15}NH$_4$Cl (Prochemicals Limited, NJ; 95.4 atom %) with 8.0 g (0.20 mol) of sodium hydroxide in 6 mL of water. This solution was distilled under reduced pressure into the pyrolysis tube. The reactants were degassed, sealed under vacuum, and heated in a stainless-steel bomb to 135 °C for 18 h. The tube was then opened; the contents were dissolved in ether, dried (K$_2$CO$_3$), and concentrated, affording 8.2 g of a yellow oil. Recrystallization from petroleum ether at −78 °C gave 7.0 g (62%) of **8** as white needles: mp 37–38 °C (lit.[17] mp 36 °C); NMR (CDCl$_3$) δ 1.22 (d, 12, J = 2 Hz), 2.22 (s, 4).

2,2,6,6-Tetramethylpiperidine-^{15}*N* (9). A total of 7.0 g (0.45 mol) of **8** was stirred with 10 g of potassium hydroxide, 9.3 mL of hydrazine hydrate, and 2.0 mL of water in 67 g of triethylene glycol at reflux for 2 h. The product was distilled (bp 96–112 °C), extracted with ether, and dried (Na$_2$SO$_4$), affording 4.5 g (72%) of a clear liquid **9**: bp 145–147 °C (lit.[11] bp 151–152 °C (750mmHg)); NMR (CDCl$_3$) δ 1.12 (d, 12, J = 2 Hz), 1.3 (m, 4), 1.6 (m, 2).

1-Nitroso-2,2,6,6-tetramethylpiperidine-^{15}*N*$_2$ (10). A solution of 1.5 g (0.011 mol) of **9** in 13 mL of a 6.8% solution of aqueous hydrochloric acid was heated to 95 °C. To this was added 1.5 g (0.021 mol) of Na^{15}NO$_2$ (Prochemicals Limited, NJ; 95.5 atom %) in 8 mL of water. The solution was stirred at 95 °C for 48 h. The reaction mixture was allowed to cool, extracted with ether, washed with 10% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride, and dried (Na$_2$SO$_4$). The ethereal layer was concentrated, affording 1.2 g (64%) of a yellow oil, **10**: NMR (CDCl$_3$) δ 1.40 (d, 6, J = 2 Hz), 1.62 (d, 6, J = 2 Hz), 1.7 (m, 6).[12]

1-Amino-2,2,6,6-tetramethylpiperidine-^{15}*N*$_2$ (4). A solution of 1.2 g (7.0 mmol) of **10** in 4 mL of dry ether was added dropwise to 580 mg (15.3 mmol) of lithium aluminum hydride in 17 mL of 1:1 di-*n*-butyl ether–diethyl ether. The temperature was slowly raised to 95 °C with distillation of solvent; the temperature was then maintained at 95 °C for 3 h. The slurry was cooled to 0 °C, excess lithium aluminum hydride was quenched with water, and 25 mL of ether was added. The layers were separated, and the aqueous layer was washed with ether. The combined ether layers were extracted with 10% aqueous hydrochloric acid. The aqueous layer was made basic with 20% aqueous sodium hydroxide. This was extracted with ether, dried (Na$_2$SO$_4$), and concentrated, affording 1.1 g of a clear oil. This was further purified by preparative VPC (Pennwalt, 180 °C) affording a 70% yield of pure 1-amino-2,2,6,6-tetramethylpiperidine-^{15}*N*$_2$ (**4**). NMR (CDCl$_3$): δ 1.05 (d, J = 2 Hz, 12), 1.5 (s, 6), 2.8 (br s, 2).[12]

***N*-(2,2,6,6-Tetramethylpiperidyl)nitrene-^{15}*N*$_2$ (1a).** To 20 mL of anhydrous dimethyl ether, cooled to −78 °C, was added 191 mg (1.9 mmol) of triethylamine and 300 mg (1.9 mmol) of 1-amino-2,2,6,6-tetramethylpiperidine-^{15}*N*$_2$ (**4**) with the aid of a syringe. To this was added 3.4 g (19 mmol) of nickel peroxide[18] through a solid addition funnel with stirring over 5 min. The reaction mixture was stirred at −78 °C for 2 h, then transferred through a Teflon tube to a cooled (−78 °C) jacketed filter funnel, and filtered into a three-necked flask cooled to −78 °C. The clear purple filtrate was concentrated (~1 M) and transferred into a 10-mm NMR tube for low-temperature (−90 °C) ^{15}N NMR studies.

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(17) Francis, F. J. *J. Chem. Soc.* **1927**, 2897.

(18) Nickel peroxide was prepared and the oxygen content determined by the method of Nakagawa.[19] Activation of nickel peroxide prepared in this manner with 6% sodium hypochlorite solution yielded a dark solid with an activity of (3.9–4.5) × 10^{-3} g atom of oxygen/g of nickel peroxide.

(19) Nakagawa, K.; Konaka, R.; Nakata, T. *J. Org. Chem.* **1962**, *27*, 1597.

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^{13}C NMR Spectroscopic Study of the Application of the "Tool of Increasing Electron Demand" to the 7-Aryl-7-norbornenyl, 7-Aryl-7-norbornyl, 2-Aryl-2-bicyclo[2.1.1]hexyl, 1-Aryl-1-cyclobutyl, and 3-Aryl-3-nortricyclyl Cations[1]

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Abstract: The "tool of increasing electron demand", coupled with ^{13}C NMR spectroscopy as the structural probe, was used to study the nature of a series of aryl-substituted carbocations of continuing interest such as the 7-aryl-7-norbornenyl, 7-aryl-7-norbornyl, 2-aryl-2-bicyclo[2.1.1]hexyl, 1-aryl-1-cyclobutyl, and 3-aryl-3-nortricyclyl cations. This study showed structural changes in the 7-aryl-7-norbornenyl cation exclusively due to the onset of π participation even with the strongly electron-releasing *p*-methoxyphenyl substituent. It also showed the onset of increased cyclopropyl conjugation in 3-aryl-3-nortricyclyl cations with the highly electron-demanding 4-trifluoromethyl and 3,5-bis(trifluoromethyl)phenyl groups. The method is, however, not sensitive enough to detect structural changes in the 1-aryl-1-cyclobutyl and 2-aryl-2-bicyclo[2.1.1]hexyl cations whose parent systems (cyclobutyl and 2-bicyclo[2.1.1]hexyl cations) have been interpreted to involve partial or full σ bridging. The inability to detect subtle structural changes in these systems demonstrates the ineffectiveness of the tool in related solvolytic studies unless the changes are very significant.

The tool of increasing electron demand was originally applied by Gassman, Richey, and Winstein[2] to measure the electron demand of the electron-deficient carbocationic center in the 7-aryl-7-norbornenyl cations **1**. It has since become increasingly

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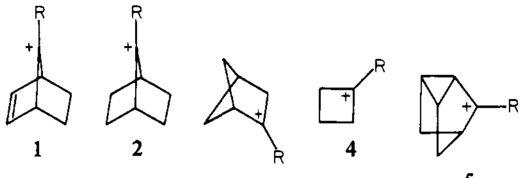

1 2 3 4 5

R = C_6H_5, C_6F_5, 4-$(CH_3)C_6H_4$, 3-$(CH_3)C_6H_4$, 4-$(OCH_3)C_6H_4$, 4-$(CF_3)C_6H_4$, 3,5-$(CF_3)_2C_6H_3$

important in probing the nature of cationic species involved in both solvolytic (studied particularly by Brown[3-5]) and stable ion studies.[6-10] The method, coupled with ^{13}C NMR spectroscopy as a probe, has given clear evidence for the onset of nonclassical σ delocalization in the 2-aryl-2-norbornyl cations[8,9] and π participation in the 2-aryl-5-norbornenyl[9] cations in superacids.

We now wish to report the application of the tool of increasing electron demand coupled with ^{13}C NMR spectroscopy in the investigation of the nature of long-lived carbocations of continuing interest such as the 7-aryl-7-norbornenyl, 2-aryl-2-bicyclo[2.1.1]hexyl, and 1-aryl-1-cyclobutyl cations. For comparison we have also studied the 7-aryl-7-norbornyl and 3-aryl-3-nortricyclyl cations.

Results and Discussion

The advantage of ^{13}C NMR over ^{1}H NMR spectroscopy as a probe to study the structure of carbocations has been discussed previously.[8,9] Farnum and co-workers[9] in a recent paper demonstrated that the ^{13}C chemical shifts of the cationic carbons of tertiary aryl substituted classical cations (with both electron-releasing and electron-withdrawing groups) relate to each other in a linear fashion. Their study is in accord with our use of the 1-aryl-1-cyclopentyl cations as the model classical system to probe into the nature of 2,5-diaryl-2,5-norbornyl dications,[10] which were found to be typical trivalent phenylcarbenium ions. In the present study a similar approach was taken. However, no attempts are made to correlate the chemical shifts of the studied cations with substituent constants, such as the σ^+ values[11] derived from solvolytic studies. The σ^+ substituent constants do not properly reflect[20a] the greater electron demand of carbocations in nonnucleophilic superacid media. Brown and co-workers[12b] have recently developed $\sigma_C{}^+$ substituent constants which are claimed to take into account the true electron demand of a carbocation center in nonnucleophilic superacid media. Since these $\sigma_C{}^+$ constants show a linear relationship with the ^{13}C NMR chemical shifts of the cationic carbon of 1-aryl-1-cyclopentyl cations,[9] their approach[12b] essentially is an extension[12c] of the previously employed method of Farnum[9] and Olah.[10]

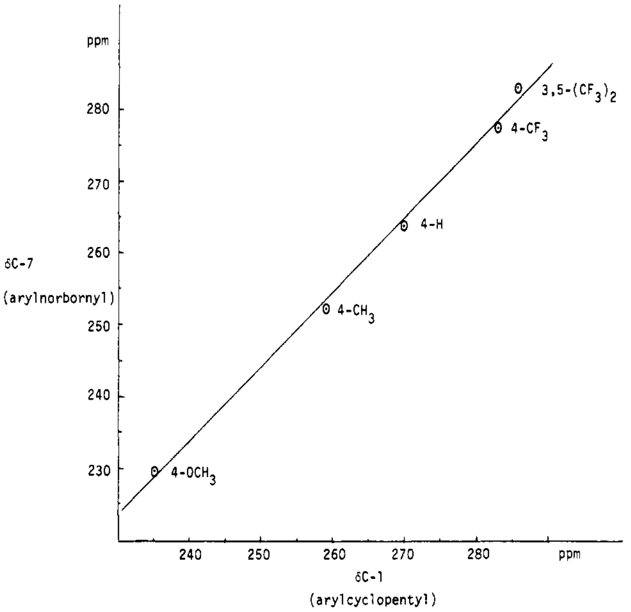

Figure 1. Correlation of the ^{13}C NMR chemical shifts of the cationic carbons in the 7-aryl-7-norbornyl and 1-aryl-1-cyclopentyl cations.

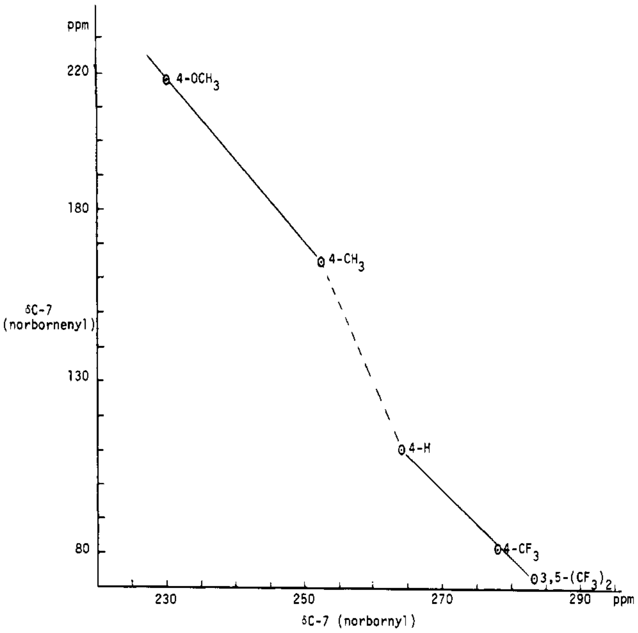

Figure 2. Correlation of the ^{13}C NMR chemical shifts of the cationic carbons in the 7-aryl-7-norbornenyl and 7-aryl-7-norbornyl cations.

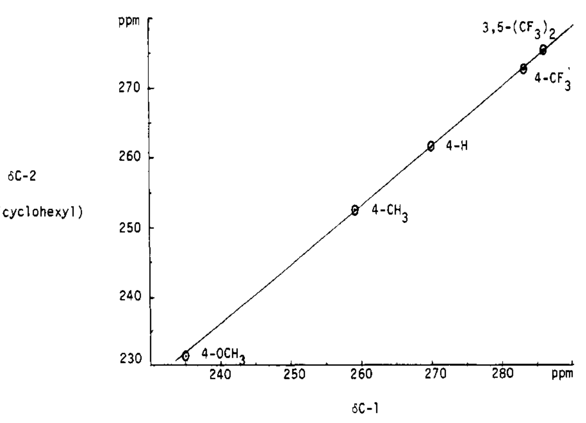

Figure 3. Correlation of the ^{13}C NMR chemical shifts of the cationic carbons in the 2-aryl-2-bicyclo[2.1.1]hexyl and 1-aryl-1-cyclopentyl cations.

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(1) Stable Carboncations, 231. For part 230 see: Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Am. Chem. Soc.* **1980**, *102*, 6127–6130.

(2) (a) Gassman, P. G.; Fentiman, A. F., Jr.. *J. Am. Chem. Soc.* **1969**, *91*, 1545–1546; **1970**, *92*, 2549–2551. (b) Richey, H. G., Jr.; Nichols, D.; Gassman, P. G.; Fentiman, A. F., Jr.; Winstein, S.; Brookhart, M.; Lustgarten, R. K. *Ibid.* **1970**, *92*, 3783–3784.

(3) For a recent account of solvolytic studies see: Brown, H. C. (Commentary by Schleyer, P. v. R.) "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.

(4) Brown, H. C.; Rao, C. G. *J. Org. Chem.* **1979**, *44*, 133–136.

(5) Brown, H. C.; Rao, C. G. *J. Org. Chem.* **1979**, *44*, 3536–3540 and references cited therein.

(6) Farnum, D. G.; Wolf, A. D. *J. Am. Chem. Soc.* **1974**, *96*, 5166–5174.

(7) Farnum, D. G.; Botto, R. E. *Tetrahedron Lett.* **1975**, 4013–4016.

(8) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 5683–5687.

(9) (a) Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847–3855. (b) We have been informed that Professor D. G. Farnum is also carrying out related studies which will be published independently.

(10) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Am. Chem. Soc.* **1980**, *102*, 6127–6130.

(11) Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, 35–148.

(12) (a) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1978**, *31*, 1209–1231. (b) Professor H. C. Brown is thanked for communicating preliminary results concerning his new $\sigma_C{}^+$ constants. (c) For a comprehensive evaluation of ^{13}C NMR chemical shifts and $\sigma_C{}^+$ substituent constants, see G. A. Olah, A. L. Berrier, and G. K. S. Prakash, *Proc. Natl. Acad. Sci. U.S.A.*, in press.

Table I. ^{13}C NMR Spectroscopic Data[a] of 7-Aryl-7-norbornenyl Cations in FSO$_3$H/SO$_2$ClF Solution at −80 °C

	δ				
carbocation	C-1, C-4	C-2, C-3 (J, Hz)	C-5, C-6	C-7	others[b]
1-4-(OCH$_3$)C$_6$H$_4$	47.3	140.0 (183.0)	23.9	218.9	C$_i$, 121.9; C$_p$, 183.7; C$_o$, 149.9; C$_m$, 121.9; OCH$_3$, 61.2
1-4-(CH$_3$)C$_6$H$_4$	49.8	142.7 (191.5)	23.1	165.4	C$_i$, 118.7; C$_p$, 158.5; C$_o$, 138.9; C$_m$, 132.7; CH$_3$, 23.1
1-C$_6$H$_5$	51.9	140.1 (191.6)	23.3	109.8	C$_i$, 120.2; C$_p$, 136.4; C$_o$, 133.3; C$_m$, 130.0
1-4-(CF$_3$)C$_6$H$_4$	55.4	138.8 (197.5)	25.0	81.2	C$_i$, 125.9; C$_p$, 135.8 (Q = 33.4 Hz); C$_o$, 132.8; C$_m$, 127.4; CF$_3$, 124.5 (Q = 286.7 Hz)
1-3,5-(CF$_3$)$_2$C$_6$H$_3$	56.4	138.1 (196.0)	25.4	73.1	C$_i$, 125.3; C$_p$, 132.2; C$_o$, 128.0; C$_m$, 133.8 (Q = 34.8 Hz); CF$_3$, 123.4 (Q = 270.1 Hz)

[a] Chemical shifts are in ppm from external capillary tetramethylsilane. [b] Here and in the following tables the abbreviations used are as follows: *i*, ipso; *p*, para; *m*, meta; *o*, ortho.

Table II. ^{13}C NMR Spectroscopic Data[a] of 7-Aryl-7-norbornyl Cations in FSO$_3$H/SO$_2$ClF or SbF$_5$/SO$_2$ClF Solution at −80 °C

	δ			
carbocation	C-1, C-4	C-2, C-3, C-5, C-6	C-7	others
2-4-(OCH$_3$)C$_6$H$_4$	41.7	27.3	229.9	C$_p$, 184.0; C$_o$, 149.4; C$_i$, 125.7; C$_m$, 120.8; OCH$_3$, 60.3
2-4-(CH$_3$)C$_6$H$_4$	43.2	26.9	252.5	C$_p$, 177.7; C$_o$, 146.9; C$_m$, 135.0; C$_i$, 130.4; CH$_3$, 25.7
2-C$_6$H$_5$	44.2	26.9	263.9	C$_p$, 158.6; C$_o$, 147.6; C$_m$, 134.0; C$_i$, 132.7
2-4-(CF$_3$)C$_6$H$_4$	46.3	27.1	277.8	C$_p$, 153.3 (Q = 34.9 Hz); C$_o$, 147.9; C$_i$, 134.7; C$_m$, 130.4; CF$_3$, 122.9 (Q = 275.7 Hz)
2-3,5-(CF$_3$)$_2$C$_6$H$_3$	47.4	27.2	283.1	C$_p$, 148.1; C$_o$, 145.7; C$_m$, 137.0 (Q = 36.4 Hz); CF$_3$, 122.5 (Q = 273.4 Hz)

[a] Chemical shifts are in ppm from external capillary tetramethylsilane.

Table III. ^{13}C NMR Spectroscopic Data[a] of 2-Aryl-2-bicyclo[2.1.1]hexyl Cations in FSO$_3$H/SO$_2$ClF or SbF$_5$/SO$_2$ClF Solution at −80 °C

	δ						
carbocation	C-1	C-2	C-3	C-4	C-5	C-6	others
3-4-(OCH$_3$)C$_6$H$_4$	59.5	231.4	42.8	31.1	47.6	47.6	C$_i$, 129.7; C$_p$, 181.5; C$_o$,C$_o'$, 147.6, 146.3; C$_m$,C$_m'$, 119.9, 119.2; OCH$_3$, 59.0
3-4-(CH$_3$)C$_6$H$_4$	63.3	252.4	45.6	37.0	50.2	50.2	C$_i$, 135.5; C$_p$, 172.6; C$_o$, 142.4; C$_m$, 134.3; CH$_3$, 25.2
3-C$_6$H$_5$	65.0	261.3	46.3	36.2	50.9	50.9	C$_i$, 135.4; C$_p$, 153.6; C$_o$,C$_o'$, 143.4, 142.1; C$_m$,C$_m'$, 132.3, 132.1
3-4-(CF$_3$)C$_6$H$_4$	70.0	272.5	49.4	37.1	54.6	54.6	C$_i$, 130.0; C$_p$, 156.7 (Q = 38.5 Hz); C$_o$,C$_o'$, 144.1, 142.9; C$_m$, 129.3; CF$_3$, 123.1 (Q = 291.4 Hz)
3-3,5-(CF$_3$)$_2$C$_6$H$_3$	72.5	275.2	50.5	37.6	56.6	56.6	C$_i$, 133.9; C$_p$, 143.6; C$_o$,C$_o'$, 142.1, 142.0; C$_m$, 134.3 (Q = 39.1 Hz); CF$_3$, 122.9 (Q = 273.1 Hz)

[a] Chemical shifts are in ppm from external capillary tetramethylsilane.

Table IV. ^{13}C NMR Spectroscopic Data[a] of 1-Aryl-1-cyclobutyl Cations in SbF$_5$/SO$_2$ClF Solution at −80 °C

	δ			
carbocation	C-1	C-2, C-4	C-3	others
4-4-(OCH$_3$)C$_6$H$_4$	234.6	39.3	16.8	C$_p$, 183.1; C$_i$, 132.2; C$_o$, 145.3; C$_m$, 120.0; OCH$_3$, 60.0
4-4-(CH$_3$)C$_6$H$_4$	259.5	42.8	17.1	C$_p$, 175.9; C$_o$, 141.8; C$_i$, 136.3; C$_m$, 134.0; CH$_3$, 25.5
4-C$_6$H$_5$	271.7	45.0	17.5	C$_i$, 138.5; C$_o$, 142.3; C$_m$, 133.2; C$_p$, 157.4
4-3-(CH$_3$)C$_6$H$_4$	269.7	44.5	17.4	C$_p$, 158.3; C$_m$(CH$_3$), 144.3; C$_o$, 141.5, 139.9; C$_m$, 132.8; C$_i$, 131.3
4-4-(CF$_3$)C$_6$H$_4$[b]	285.3	47.4	16.9	C$_i$, 139.7; C$_o$, 142.6; C$_p$, 152.1 (Q = 34.7 Hz); C$_m$, 129.7; CF$_3$, 122.8 (Q = 278.7 Hz)
4-3,5-(CF$_3$)$_2$C$_6$H$_3$[c]	290.1	50.5	17.9	C$_i$, 146.4; C$_p$, 140.5; C$_o$, 137.7; C$_m$, 137.3 (Q = 35.7 Hz); CF$_3$, 122.9 (Q = 273.4 Hz)
4-C$_6$F$_5$	277.8	52.3	23.2	C$_p$, 162.2 (d, 297.6 Hz); C$_o$, 153.5 (d, 290.9 Hz); C$_m$, 139.7 (d, 259.3 Hz); C$_i$, 118.1

[a] Chemical shifts are in ppm from external capillary tetramethylsilane. [b] Taken at −114 °C. [c] Taken at −123.4 °C.

Table V. ^{13}C NMR Spectroscopic Data[a] of 3-Aryl-3-nortricyclyl Cation in FSO$_3$H/SO$_2$ClF or SbF$_5$/SO$_2$ClF Solution at −80 °C

	δ							
carbocation	C-1	C-2	C-3	C-4	C-5	C-6	C-7	others
5-4-(OCH$_3$)C$_6$H$_4$	43.4	38.9	235.0	34.0	38.9	43.4	38.9	C$_i$, 128.3; C$_p$, 179.9; C$_o$, 145.0; C$_m$,C$_m'$, 120.3, 118.4; OCH$_3$, 59.3
5-4-(CH$_3$)C$_6$H$_4$	54.7	42.2	251.1	40.1	40.1	54.7	40.1	C$_i$, 132.4; C$_p$, 167.5; C$_o$, 140.4; C$_m$,C$_m'$, 134.0, 134.2; CH$_3$, 25.2
5-3-(CH$_3$)C$_6$H$_4$	59.9	46.1	256.5	40.6	40.6	59.9	40.6	C$_i$, 134.6; C$_p$, 151.2; C$_m$(CH$_3$), 143.8; C$_o$,C$_o'$, 139.6, 137.5; C$_m$, 132.4; CH$_3$, 20.9
5-C$_6$H$_5$[b]	61.4	47.1	257.1	40.4	40.8	61.4	40.8	C$_i$, 134.1; C$_p$, 149.8; C$_o$, 139.6; C$_m$,C$_m'$, 132.6, 132.1
5-4-(CF$_3$)C$_6$H$_4$	73.5	56.1	260.5	41.7	42.6	73.5	42.6	C$_i$, 135.9; C$_p$, 151.5 (Q = 34.3 Hz); C$_o$,C$_o'$, 144.7, 144.1; C$_i$, 135.6; C$_m$, 129.9; CF$_3$, 123.2 (Q = 279.8 Hz)
5-3,5-(CF$_3$)$_2$C$_6$H$_3$	80.5	61.1	259.0	42.2	43.4	80.5	43.4	C$_i$, 134.6; C$_p$, 138.3; C$_o$,C$_o'$, 136.6, 136.4; C$_m$, 135.3 (Q = 44.9 Hz); CF$_3$, 123.3 (Q = 273.3 Hz)

[a] Chemical shifts are in ppm from external capillary tetramethylsilane. [b] In FSO$_3$H:SbF$_5$(4:1)/SO$_2$ClF.

The ^{13}C NMR chemical shifts of the studied carbocations are shown in Tables I–V. The chemical shifts were assigned on the basis of off-resonance–decoupling experiments. Figures 1–7 depict comparative plots of the ^{13}C NMR chemical shifts of the studied cations, including those with the reported values of the 1-aryl-1-cyclopentyl cations.[9]

7-Aryl-7-norbornenyl Cations. The onset of π participation in the 7-aryl-7-norbornenyl system **1-R** both in solvolysis and under

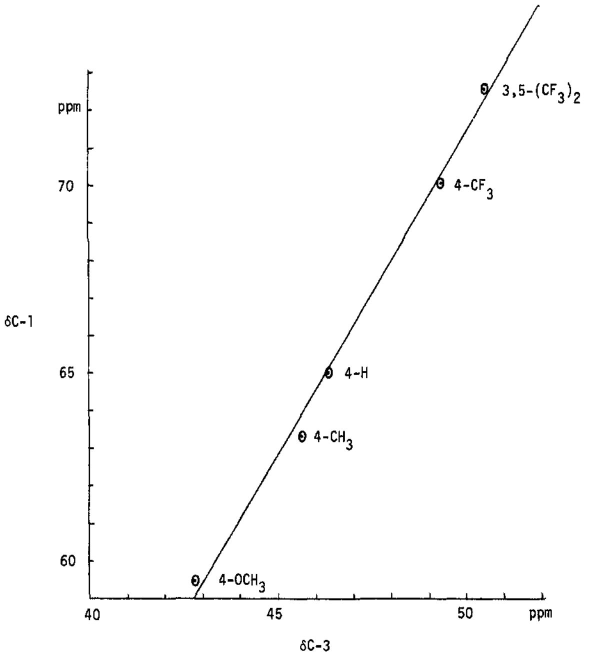


Figure 4. Correlation of the ^{13}C NMR chemical shifts of C-1 and C-3 carbons in the 2-aryl-2-bicyclo[2.1.1]hexyl cations.

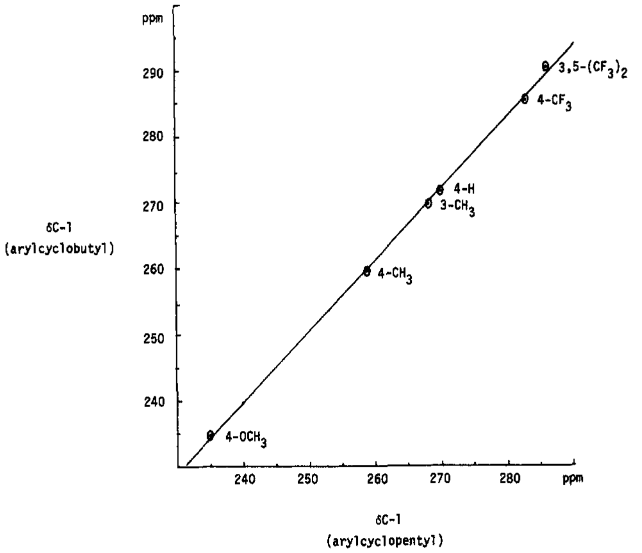


Figure 5. Correlation of the ^{13}C NMR chemical shifts of the cationic carbons in the 1-aryl-1-cyclobutyl and 1-aryl-1-cyclopentyl cations.

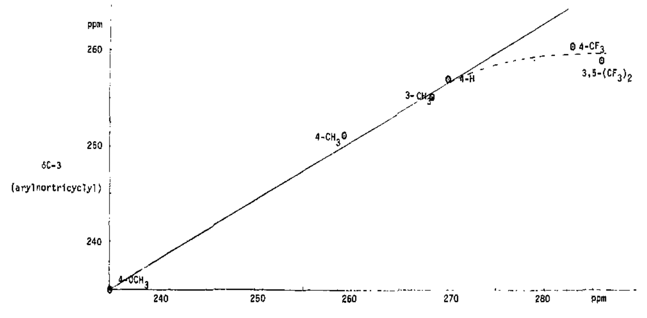


Figure 6. Correlation of the ^{13}C NMR chemical shifts of the cationic carbons in the 3-aryl-3-nortricyclyl and 1-aryl-1-cyclopentyl cations.

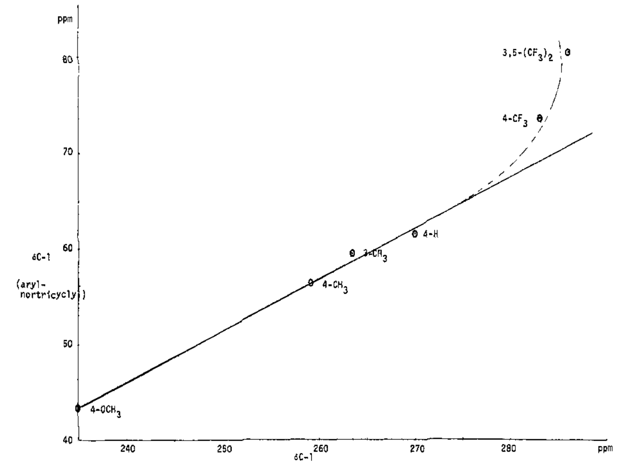


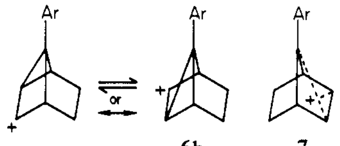
Figure 7. Correlation of the ^{13}C NMR chemical shifts of the C-1 carbons of 3-aryl-3-nortricyclyl cations vs. the cationic carbons of 1-aryl-1-cyclopentyl cations.

stable ion conditions was demonstrated by Gassman, Richey, and Winstein.[2] A dramatic increase in the slope of the Hammett plot of the rate constants in the case of aryl groups with less electron-releasing substituents than 4-methoxy and 4-dimethylamino led them to suggest that these systems were solvolyzing with π participation. The ^{1}H NMR spectrum of the 4-methoxyphenyl cation **1**-4-(OCH$_3$)C$_6$H$_4$ was found to be radically different from that of analogous ions showing π participation, indicating that under stable ion conditions, the 4-methoxyphenyl cation behaved as a classical ion. More recently, Farnum and co-workers[9] have replotted the ^{1}H NMR data of the vinylic protons and the solvolytic rate constants vs. the σ^+ substituent constants and showed that while the onset of π participation occurred with the *p*-tolyl derivative in superacidic solutions, the onset of π participation in the less electron-demanding transition state for solvolysis occurred with the less electron-demanding *p*-methoxyphenyl substituent. It was also realized that the vinylic hydrogen chemical shifts in the 7-aryl-7-norbornenyl cations **1**-R were relatively insensitive to the nature of the aryl group. Since ^{13}C NMR spectroscopy can directly observe the cationic carbon, we felt it was of interest to obtain the complete ^{13}C NMR data for a series of substituted 7-aryl-7-norbornenyl cations **1**-R. For comparison we also determined the ^{13}C NMR shifts of the saturated analogous 7-aryl-7-norbornyl cations **2**-R. The chemical shifts are given in Tables I and II.

Before a meaningful comparison could be made between cations **1**-R and **2**-R, it was necessary to determine the nature of the latter by comparing it with the model classical system, the 1-aryl-1-cyclopentyl cations. The C-7 cationic carbon chemical shifts in **2**-R range from $\delta(^{13}C)$ 229.9 in the case of the *p*-methoxy substituent to $\delta(^{13}C)$ 283.1 for the strongly electron-withdrawing 3,5-bis(trifluoromethyl) group. The corresponding C–1 cationic chemical shifts in the 1-aryl-1-cyclopentyl cations[9] range from $\delta(^{13}C)$ 235.0 to $\delta(^{13}C)$ 286.0. A plot of the C-7 cationic carbon chemical shifts of the 7-aryl-7-norbornyl cations **2**-R against those of the model 1-aryl-1-cyclopentyl system[9] shows an excellent linear relationship (Figure 1, $r = 0.998$) confirming the classical nature of ions **2**-R.

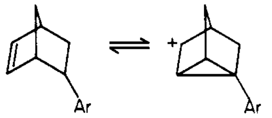
Having established the classical phenyl carbenium ion nature of cations **2**-R, we plotted the C-7 cationic carbon chemical shifts against those of the 7-aryl-7-norbornenyl cations **1**-R (Figure 2). Not only does the plot reveal apparent breaks but it also has a negative slope indicative of substantial π interaction in the cations **1**-R. As the electron demand of the aryl group is progressively increased, the C-7 cationic carbon shift undergoes a gradual shielding effect due to increasing π participation. The observed C-7 chemical shifts for cations **1**-R with aryl substituents 4-OCH$_3$, 4-CH$_3$, 4-H, 4-CF$_3$, and 3,5-(CF$_3$)$_2$ are $\delta(^{13}C)$ 218.9, 165.4, 109.8, 81.2, and 73.1, respectively. However, over the range of substituents studied, the vinylic carbon chemical shifts remain relatively insensitive. A spread of only 4.1 ppm is observed for the vinylic carbons whereas a spread of 138 ppm is seen in the case of the C-7 cationic carbons indicating the questionable reliability of employing either the ^{13}C NMR data of these vinylic carbons or the previously used ^{1}H NMR data of the vinylic protons to determine structural changes. Moreover, the present study demonstrates that the 4-methoxyphenyl substituted **1**-4-$(OCH_3)C_6H_4$ is of diminished classical nature due to substantial π participation than is the case of its saturated analogue **2**-4-$(OCH_3)C_6H_4$. There is a 10-ppm shielding effect observed for the former cation over the latter. It is thus indicated (from Figure 2) that the onset of π participation in the cations **1**-R, under the strongly electron-demanding conditions studied (in superacids), occurs with the 4-methoxyphenyl substitutent and gradually increases beyond the 3,5-bis(trifluoromethyl)phenyl substituent.

A condition labeled[9] "saturation of π-participation" where the double bond has given all it could give (involving structures such as **6a** and **6b** either as a pair of resonance contributors or an equilibrating pair) is not detected in this system with the employed substituents. On the basis of observed results we feel that ions **1**-R are best represented as symmetrically bridged nonclassical structures **7**. The extent of the nonclassical nature of ions **7**, however, depends on the nature of the substituent at the C-7 position. It is significant to note that the previously investigated[13] cations **1**-H and **1**-CH_3 show substantial shielding of both the C-7 and vinylic carbon chemical shifts ($\delta(^{13}C)$ 34.0 and 71.9 for the C-7 carbons and 125.9 and 134.1 for the vinylic carbons, respectively), indicating the nonclassical nature of these ions.



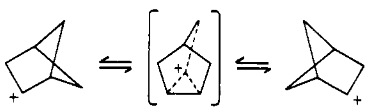
6a 6b 7

A cyclopropylcarbinyl-type resonance or equilibration such as in **6a,b** for the parent ion is definitely ruled out on the basis of a consideration of the additivity of chemical shifts.[14] The total ^{13}C NMR chemical shift difference between the parent ion **1**-H with respect to norbornene as the model hydrocarbon is less than 0. The similar chemical shift difference between the nortricyclyl cation (a classical ion) and nortricylene is more than 500 ppm. However, in the case of the 2-aryl-5-norbornenyl cations where the magnitude of homoallylic π participation is not as extensive, Farnum and co-workers[9] accommodated the observed ^{13}C NMR chemical shifts as due to either equilibrium **8a**–**8b** or π bridging and could not distinguish one from the other.



8a 8b

2-Aryl-2-bicyclo[2.1.1]hexyl Cations. The bicyclo[2.1.1]hexyl cation 3-H was first observed[15] by Seybold, Vogel, Saunders, and Wiberg in superacidic media by ^1H NMR spectroscopy. They suggested a bridged structure **9** for the ion. Similar conclusions were drawn by Meinwald, Gassman, and Crandall from solvolytic studies.[16] In a subsequent ^{13}C NMR study,[17] Olah, Liang, and Jindal concluded that there is only partial σ bridging in the rapidly equilibrating ion. Brown and co-workers[18] in a solvolytic study of 2-aryl-2-bicyclo[2.1.1]hexyl cations **3**-R found an excellent log $k-\sigma^+$ relationship and a negative ρ value indicating the unimportance of σ participation in the system.



9

Saunders and Wiberg[19a] have recently restudied the parent bicyclo[2.1.1]hexyl cation by the isotopic perturbation of resonance technique (by deuterium substitution at the exchanging sites) and concluded that there is significant σ bridging in the parent ion **3**-H. The additivity of ^{13}C NMR chemical shifts[14] shows that the observed total chemical shift difference between ion **3**-H and its parent hydrocarbon bicyclo[2.1.1]hexane is 296 ppm, 100 ppm less than that found in the case of the 2-methyl-2-bicyclo-[2.1.1]hexyl cation **3**-CH_3 but about 120 ppm more than for the nonclassical 2-norbornyl cation, indicating the partially bridged nature of **3**-H. Recent work of Sorenson and Schmitz[19b] has shown that the free energy difference between cations **3**-H and **3**-CH_3 is 7–9.8 kcal/mol, compared to 5.5 and 11.4 kcal/mol for the analogous 2-norbornyl and cyclopentyl ions, also confirming the intermittent (partially bridged) nature of ion **3**-H.

In view of the conflicting conclusions reached concerning the nature of ion **3**-H, the tool of increasing electron demand was applied to the study of related 2-aryl-2-bicyclo[2.1.1]hexyl cations **3**-R.

Table III lists the ^{13}C NMR data of cations **3**-R. The cationic carbon shifts vary from $\delta(^{13}C)$ 231.4 in the case of the 4-methoxy substituent to $\delta(^{13}C)$ 275.2 for the 3,5-bis(trifluoromethyl) derivative (a chemical shift spread of 43.8 ppm). A much narrower spread of 25 ppm was observed for the homologous 2-aryl-2-norbornyl cations.[8,9] Figure 3 shows the plot of the C-2 cationic carbon shifts vs. those of the model 1-aryl-1-cyclopentyl cations.[9] An excellent linear fit is observed ($r = 0.998$), indicating the absence of the onset of any significant σ delocalization (in these aryl carbenium ions **3**-R) over the range of substituents studied. In contrast, in the case of the homologous 2-aryl-2-norbornyl cations[9] significant deviation was observed with electron-withdrawing substituents.

We have also plotted the C-1 carbon chemical shifts against those of C-3 (Figure 4). In this plot an excellent linear relationship is again observed ($r = 0.999$), demonstrating that both the C-1 and C-3 carbons in cations **3**-R experience similar neighboring group deshielding effects. If there would be any onset of σ delocalization, the C-1 chemical shift should have changed considerably compared to the C-3 carbon shifts in the case of electron-withdrawing substituents. A similar[10] study on the 2,5-diaryl-2,5-norbornyl dications also showed a linear plot of the C-1 vs. C-3 ^{13}C NMR shifts, indicating the regular phenylcarbenium ion nature of the ions. However, in the case of the 2-aryl-2-norbornyl cations, a deviation from linearity was observed in the case of more electron-demanding substituents, denoting the onset of σ delocalization.

It must be emphasized that an aryl group even with strongly electron-withdrawing substituents is still capable of charge delocalization into its 6π system. The tool of increasing electron demand consequently can be successful only if there are significant changes in the structure of the cations due to substantial σ or π interactions with the electron-deficient centers.

1-Aryl-1-cyclobutyl Cations. The nature of the cationic intermediates involved in cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl interconversions under solvolytic as well as stable ion conditions is of substantial continuing interest.[20-22] In recent NMR structural studies, the structures of cyclobutyl (cyclo-

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[13] Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 6803–6806.

[14] Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683–691.

[15] Seybold, G.; Vogel, P.; Saunders, M.; Wiberg, K. B. *J. Am. Chem. Soc.* **1973**, *95*, 2045–2047.

[16] (a) Meinwald, J.; Gassman, P. G. *J. Am. Chem Soc.* **1963**, *85*, 57–59. (b) Meinwald, J.; Crandall, J. K. *Ibid.* **1966**, *88*, 1292–1301.

[17] Olah, G. A.; Liang, G.; Jindal, S. P. *J. Am. Chem. Soc.* **1976**, *98*, 2508–2511.

[18] Brown, H. C.; Ravindranathan, M.; Rao, C. G. *J. Am. Chem. Soc.* **1977**, *99*, 2359–2361.

[19] (a) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *J. Am. Chem. Soc.* **1977**, *99*, 8072–8073. (b) Schmitz, L. R.; Sorensen, T. S. *Ibid.* **1980**, *102*, 1645–1648.

[20] For reviews on cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl cations, see: (a) Richey, G. "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R. Eds.; Wiley-Interscience, New York, 1972; Vol III, Chapter 25. (b) Wiberg, K. B.; Hess, B. A.; Ashe, A. J. *Ibid.*; Chapter 26.

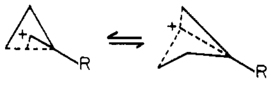
[21] For more recent investigations of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl cations, see: (a) Kelly, D. P.; Underwood, G. R.; Barron, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 3106–3111. (b) Olah, G. A.; Spear, R. J.; Hilberty, P. C.; Hehre, W. J. *Ibid.* **1976**, *98*, 7470–7475.

[22] Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1977**, *99*, 6687-6693.

propylcarbinyl) **10** and 1-methylcyclobutyl (α-methylcyclopropylcarbinyl) **11** cations have been reinterpreted to involve nonclassical bicyclobutonium ions such as **12** and **13** respectively.[23,24] Also, the total ^{13}C NMR chemical shift difference between cations **10** and **11** and their respective hydrocarbons indicated the nonclassical nature of these ions.[14] Saunders and Siehl[25] have demonstrated the deuterium isotope effect on the ion **10** and concluded that the effect clearly indicates the bicyclobutonium form **12** as the preferred structure.

$C_4H_7^+$ $C_5H_9^+$

10 **11**

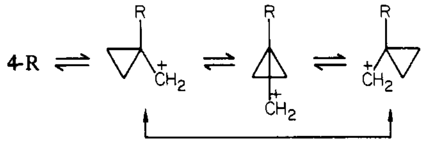


12, R = H

13, R = CH_3

In contrast, the 1-phenyl-1-cyclobutyl cation **4**-C_6H_5 is a static classical ion whose ^{13}C NMR chemical shifts (Table IV) compare well with those of the 1-phenyl-1-cyclopentyl and 1-phenyl-1-cyclohexyl cations.[9,26] In order to further explore the nature of cations **10** and **11**, we altered the electron demand at the cationic center by varying the nature of the substituents on the phenyl ring. The ^{13}C NMR chemical shifts of the substituted 1-aryl-1-cyclobutyl cations **4**-R are listed in Table IV.

Whereas **4**-C_6H_5, **4**-C_6F_5, **4**-4-$(CH_3)C_6H_4$, **4**-3-$(CH_3)C_6H_4$, and **4**-4-$(OCH_3)C_6H_4$ show static classical carbocation nature over the temperature range studied (0 to −140 °C), the (4-(trifluoromethyl)phenyl)cyclobutyl and (3,5-bis(trifluoromethyl)-phenyl)cyclobutyl cations **4**-4-$(CF_3)C_6H_4$ and **4**-3,5-$(CF_3)_2C_6H_3$ were found to be equilibrating ions.[24] They equilibrate through the related but practically unpopulated (in the Boltzman distribution) cyclopropylcarbinyl cations **14** which average the methylene carbons. The ^{13}C NMR shift of the cationic carbon in **4**-4-$(CF_3)C_6H_4$ (at −60 °C) was $\delta(^{13}C)$ 286.4 while that for **4**-3,5-$(CF_3)_2C_6H_3$ (at −34 °C) was $\delta(^{13}C)$ 284.7. The average methylene peaks were observed at $\delta(^{13}C)$ 39.6 (at −60 °C) and $\delta(^{13}C)$ 37.8 (at −34 °C), respectively. Both mono- and bis(trifluoromethyl)-substituted arylcyclobutyl cations were frozen out to the static cyclobutyl system at −114 and −123 °C, respectively. The barriers for the equilibrating processes were estimated[27] from the coalescence temperatures and were found to be $\Delta G^{\ddagger}_{203\ K} = 8.8 \pm 0.5$ kcal/mol for **4**-4-$(CF_3)C_6H_4$ and $\Delta G^{\ddagger}_{173\ K} = 7.4 \pm 0.5$ kcal/mol for **4**-3,5-$(CF_3)_2C_6H_3$. The completely frozen-out systems showed the cationic carbon shifts at $\delta(^{13}C)$ 285.3 and 290.1 for the mono- and bis(trifluoromethyl)-substituted arylcyclobutyl cations, indicating a slight temperature-induced change in the chemical shifts. It is somewhat surprising that the (pentafluorophenyl)cyclobutyl cation **4**-C_6F_5 behaved as a static species up to 0 °C, demonstrating the lack of sufficient electron demand at the cationic carbon to set up a cyclopropylcarbinyl-type equilibria. The ortho and para fluorine atoms, besides their inductive electron-withdrawing ability, also delocalize charge through resonance interaction with the nonbonded electron pair.



14, R = 4-$(CF_3)C_6H_4$, 3,5-$(CF_3)_2C_6H_3$

Analysis of the data in Table IV shows a spread of 55 ppm for the cationic carbons ranging from 4-OCH_3 to 3,5-$(CF_3)_2$ substituents on the aryl ring. Figure 5 shows a plot of the ^{13}C NMR chemical shifts of the cationic carbons of ions **4**-R against those of the 1-aryl-1-cyclopentyl cations.[9] An excellent linear fit is observed over the range of substituents studied ($r = 0.999$), indicating no significant onset of σ delocalization in these aryl-substituted systems. Even with the strongly electron-withdrawing 4-CF_3 and 3,5-$(CF_3)_2$ groups on the aryl ring, the cations **4**-4-$(CF_3)C_6H_4$ and **4**-3,5-$(CF_3)_2C_6H_3$ do not show deviation from linearity (Figure 5), indicating the limited applicability of the applied method even under strongly electron-demanding long-lived stable ion conditions. For the reasons discussed we feel that the current study does not alter previous conclusions[23,24] on the nonclassical nature of cations **10** and **11**.

3-Aryl-3-nortricyclyl Cations. The cyclopropane ring in the geometrically rigid 3-nortricyclyl cation **5**-H[28] is situated in a favored bisected configuration[29,30] toward the electron-deficient center for maximum charge delocalization. A ^{1}H and ^{13}C NMR spectroscopic investigation by Olah and Liang showed that secondary and tertiary 3-nortricyclyl cations **5**-R are essentially classical cations with substantial charge delocalization into the rigid cyclopropane skeleton. The extent of the charge delocalization into the cyclopropane ring was indicated by the degree of deshielding of the β-carbons (i.e., the C-1 and C-6 carbons). In fact, the C_β chemical shift has been used as a reliable indicator of the extent of the charge delocalization in several types of cyclopropylcarbinyl cations such as the dehydroadamantyl,[31] dehydrohomoadamantyl,[32] homonortricyclyl,[33] and benzotropylium and dihydrobenzotropylium[34] cations. Since we were interested in the relative charge-delocalizing abilities[35] of a cyclopropyl group vs. a phenyl group, the tool of increasing electron demand was applied to the 3-aryl-3-nortricyclyl cations **5**-R, in expectation of a marked increase in cyclopropyl conjugation with more electron-demanding aryl groups.

Table V contains the ^{13}C NMR chemical shifts of the 3-aryl-3-nortricyclyl cations **5**-R. The C-3 cationic carbon shifts are spread over a 25-ppm range, whereas the C_β carbons (C-1 and C-6) show a substantially larger spread of 37 ppm. A plot of the C-3 chemical shifts vs. those in the model 1-aryl-1-cyclopentyl cations[9] reveals a deviation from linearity in the case of the 4-(trifluoromethyl)- and 3,5-bis(trifluoromethyl) substituents (Figure 6). These substituents substantially shield the cationic center. However, the C_β carbons (C-1 and C-6) are significantly deshielded. This is evident from the plot of the C_β carbon chemical shifts vs. the cationic shifts of their 1-aryl-1-cyclopentyl analogues (Figure 7). When the aryl group with more electron-demanding substituents can no longer effectively accommodate the positive charge, the bent π–σ bond of the rigid cyclopropane skeleton increasingly contributes in dispersing the charge. Application of the tool of increasing electron demand thus is capable, even in the case of highly delocalized classical ions,[28] in demonstrating changes in their structure with more electron-demanding substituents.

Conclusions

The present application of the tool of increasing demand to a series of structurally differing carbocationic systems under stable-ion conditions using ^{13}C NMR spectroscopy serves as a structural probe in determing the onset of π or σ delocalization (participation), but only when such changes are considerable. As phenyl groups even with electron-withdrawing substituents still

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(23) Staral, J.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J.; Olah, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8016–8018.

(24) Olah, G. A.; Prakash, G. K. S.; Donovan, D. J.; Yavari, I. *J. Am. Chem. Soc.* **1978**, *100*, 7085–7086.

(25) Saunders, M.; Siehl, H.-U. *J. Am. Chem. Soc.* **1980**, *102*, 6868–6869.

(26) Liang, G. Ph.D. Dissertation, Case Western Reserve University, 1973.

(27) Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc. D* **1971**, 656–657 and references cited therein.

(28) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 1920–1927.

(29) Olah, G. A.; Jeuell, C. L.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 146–156.

(30) (a) Baldwin, J. E.; Foggelsong, W. D. *J. Am. Chem. Soc.* **1968**, *90*, 4311–4315. (b) Radom, L.; Pople, J. A.; Burs, V.; Schleyer, P. v. R. *Ibid.* **1970**, *92*, 6380–6382. (c) Kollmar, H.; Smith, H. O. *Tetrahedron Lett.* **1970**, 3133–3136. (d) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 302–304.

(31) Olah, G. A.; Liang, G.; Babiak, K. A.; Ford, T. M.; Goff, D. L.; Morgan, T. K., Jr.; Murray, R. K., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 1494–1500.

(32) Olah, G. A.; Liang, G.; Babiak, K. A.; Morgan, T. K., Jr.; Murray, R. K., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 576–580.

(33) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1976**, *98*, 7026–7033.

(34) Olah, G. A.; Liang, G. *J. Org. Chem.* **1975**, *40*, 2108–2116.

(35) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Org. Chem.* **1977**, *42*, 2666–2671.

can delocalize charge into the 6π system, the tool is rather coarse and therefore ineffective in the cases where structural changes are limited, including systems which have been described as partially bridged or delocalized. For the same reasons the method must be considered ineffective in the usual solvolytic studies, wherein the solvation significantly masks the true electron demand of the carbocationic center in the solvolytic transition state unless the structural change is significant (as in the case of 7-norbornenyl or pentacyclononyl system[36]).

Experimental Section

The carbocations studied in this work were generated from their alcohol precursors. The alcohols were prepared by the addition of the appropriate aryl Grignard reagent to the respective ketones in ether solution. Most of the alcohols employed in this study have been reported earlier[2,24] except those of the cyclobutyl and nortricyclyl series. All new compounds gave satisfactory analysis and spectroscopic data.

Preparation of Carbocations. Freshly distilled SbF_5 and FSO_3H were used. To the appropriate superacid dissolved in about a twofold amount of SO_2ClF at dry ice/acetone (ca. −78 °C) or petroleum ether/liquid nitrogen slush temperature (−140 °C) was slowly added, with vigorous stirring, a cooled slurry or solution of the corresponding alcohol precursor in SO_2ClF, resulting in an approximately 10% solution of the ion.

^{13}C NMR spectra were obtained with use of a Varian Associates Model FT-80 spectrometer equipped with multinuclei broad-band variable temperature probe. The chemical shifts were referenced from external capillary tetramethylsilane.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

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[36] Brown, H. C.; Ravindranathan, M. *J. Am. Chem. Soc.* **1977**, *99*, 299–300.

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^{17}O NMR Studies of Substituent and Hydrogen-Bonding Effects in Substituted Acetophenones and Benzaldehydes[1a]

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Abstract: ^{17}O nuclear magnetic resonance is utilized in exploring substituent effects and hydrogen-bonding interactions in ^{17}O-enriched and natural abundance aromatic carbonyl systems. Chemical shifts and line widths are presented for a wide range of mono- and polysubstituted acetophenones and benzaldehydes. The ^{17}O nuclear screening constants are highly sensitive to electronic perturbations induced by substitutent groups as indicated in chemical shift ranges of 101, 60, and 13 ppm for the ortho-, para- and meta-substituted acetophenones, respectively. Intramolecular hydrogen bonding in the ortho amino and ortho hydroxy molecules results in anomalous ^{17}O chemical shifts to high field. In the case of intramolecular hydrogen-bonded compounds it is shown that for the polysubstituted acetophenones the substitutent effects are much smaller and superimposed on the dominating effect of hydrogen bonding on the ^{17}O nuclear screening. Alcohol solvents induce upfield chemical shifts in acetophenone and *m*-hydroxyacetophenone, and the degree of increased shielding is dependent on solvent concentration (acetophenone undergoes a 17-ppm upfield shift upon infinite dilution in methanol). Line widths range from approximately 300 Hz (benzaldehyde) to greater than 4 kHz (2,3,4-trihydroxyacetophenone). Rate constants for carbonyl oxygen exchange in a $H_2{}^{17}O$/dioxane mixed solvent are reported for several substituted acetophenones. A good correlation of the chemical shifts of the para-substituted acetophenones with the lowest energy electronic transition implies that $\Delta E_{n\rightarrow\pi^*}$ makes the dominant contribution to the ^{17}O nuclear screening. The ^{17}O chemical shifts are correlated with Hammett constants, IR carbonyl stretching bands, UV, and X-ray diffraction data.

Introduction

The carbonyl group can be sensitive to electronic disturbances occurring at various sites in an aromatic molecule due, in large part, to its ability to enter into conjugation with adjacent π systems. The electron distribution in the acyl function of aromatic compounds and the electronic perturbations induced by ring substitutions have been a longstanding subject of spectroscopic investigation.[2] Recent applied and theoretical studies of substituted benzaldehydes and acetophenones demonstrate an active interest in these systems.[3]

Although substituent effects on ^{13}C,[4] ^{1}H,[5] ^{14}N,[6] ^{15}N,[7] and ^{19}F[8] nuclear screening constants in aromatic systems have been documented, similar systematic studies employing ^{17}O NMR have not appeared. Despite the difficulties in working with ^{17}O (due to the ^{17}O quadrupole moment, $I = {}^5/_2$, and low natural isotopic abundance, 0.037%) several chemical shift studies have been

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[2] (a) Bentley, J. B.; Everard, K. B.; Marsden, R. J. B.; Sutton, L. E. *J. Am. Chem. Soc.* **1949**, *71*, 2957. (b) Hehre, W. J.; Radom, L.; Pople, J. A. *Ibid.* **1972**, *94*, 1496. (c) Miller, F. A.; Fateley; Witkowski, R. E. *Spectrochim. Acta, Part A* **1967**, *32A*, 891. (d) Montaudo, G.; Finoccihiaro, P.; Maravigna *J. Am. Chem. Soc.* **1971**, *93*, 4214.

[3] (a) Young, P. R.; McMahon, P. E. *J. Am. Chem. Soc.* **1979**, *101*, 4678. (b) Plesnicar, B.; Smolikova, J.; Hehlicka, V.; Exner, O. *Collect. Czech. Chem. Commun.* **1978**, *43*, 2754. (c) Barthelemy, J. F.; Jost, R.; Sommer, J. *Org. Magn. Reson.* **1978**, *11*, 438. (d) Laurence, C.; Berthelot, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, *98*. (e) Gupta, D.; Gupta, V. P. *Ind. J. Pure. Appl. Phys.* **1978**, *16*, 968.

[4] (a) Stothers, J. B.; Lauterbur, P. C. *Can. J. Chem.* **1964**, *42*, 1563. (b) Spiesecke, H.; Schneider, W. G. *J. Chem. Phys.* **1961**, *35*, 731.

[5] (a) Batts, B. D.; Parsibu, S. J.; Williams, L. R. *Org. Magn. Reson.* **1977**, *9*, 210. (b) Beeby, J.; Sternhell, T.; Hoffman-Ostenhof, T.; Pretsch, E.; Simon, W. *Anal. Chem.* **1973**, *45*, 1571. (c) Bloxsidge, J.; Jones, J. R.; Marks, R. E. *Org. Magn. Reson.* **1970**, *2*, 337.

[6] Hampson, P.; Mathias, A.; Westhead, R. *J. Chem. Soc. B* **1971**, 397.

[7] Pregosin, P. S.; Randall, E. W.; White, A. I. *J. Chem. Soc., Perkin Trans. 2* **1972**, 153.

[8] (a) Taft, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 1045. (b) Taft, R. W.; Glick, R. E.; Lewis, I. C.; Ehrenson, S. *J. Am. Chem. Soc.* **1960**, *82*, 756.

0002-7863/81/1503-1128$01.25/0