HETEROCYCLES, Vol. 18, 1982

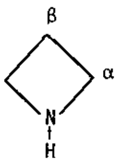
PROTONATION INDUCED CARBON-13 NMR SHIFTS IN PROTONATED CYCLIC AMINES*

Mariappan Periasamy

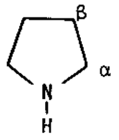
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 U.S.A.

Abstract - *Protonation induced Carbon-13 NMR chemical shifts are measured for five cyclic amines* (1-5). *The effect of sp^3 hybridized positive charge on the chemical shifts of remote carbon atoms in protonated cyclic amines is compared with the effect of sp^2 hybridized positive charge on the chemical shifts of remote carbon atoms in arylcyclic carbocations.*

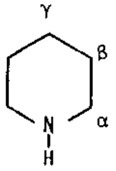
Recently, we observed that the effect of positive charge (C^+ center) on the chemical shifts of remote carbon atoms in cyclic carbocations is markedly dependent on the ring size and conformational characteristics.[1,2] It was of interest to study the effect of positive charge on the chemical shifts of remote carbon atoms in protonated cyclic amines (1-5).



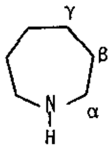
1



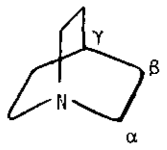
2



3



4



5

In addition to providing the effect of ring size on the protonation induced Carbon-13 NMR shifts, the data would also allow the comparison of the effect of sp^3 hybridized positive charge on the chemical shifts of remote carbon atoms in protonated cyclic amines with the effect of sp^2 hybridized positive charge on the chemical shifts of remote carbon atoms in arylcyclic carbocations.

Protonation induced Carbon-13 NMR shifts have been reported for some cyclic amines.[3] Trifluoroacetic acid was used as the medium in this study. However, it has been reported that in some cases the salts precipitated in this medium. We have observed that clear solutions of the amine (mol 10%) can be prepared in fluorosulfuric acid. The amine was added to FSO_3H in an 8-mm NMR

---

*Dedicated to Professor Herbert C. Brown for his contributions to chemistry on the occasion of his 70th birthday.

tube at -78°C and the contents were slowly warmed to 25°C with stirring. The ^{13}C NMR spectra were recorded at 25°C on a Varian CFT-20 spectrometer, using 8192 data points, a spectral width of 4000 Hz, and a pulse angle of 45°. The chemical shifts of the protonated amines are summarized in Table I, along with the shifts observed for the parent amines.

TABLE I. ^{13}C Shifts[a] of Free Imines[b] and Protonated Amines

System		Chemical Shift[c]					
		$\delta C\alpha$	$\Delta\delta C\alpha$	$\delta C\beta$	$\Delta\delta C\beta$	$\delta C\gamma$	$\Delta\delta C\gamma$
1	NH	48.1		22.1			
	NH_2^+	50.7	-2.6	19.6	+2.5		
2	NH	47.1		25.7			
	NH_2^+	48.9	-1.8	24.6	+1.1		
3	NH	47.6		27.4		25.3	
	NH_2^+	47.9	-0.3	23.5	+3.9	22.3	+3.0
4	NH	49.3		31.5		27.1	
	NH_2^+	49.6	-0.3	26.8	+4.7	25.9	+1.2
5	N	47.9		26.9		20.9	
	NH^+	49.2	-1.3	23.4	+3.5	19.7	+1.2

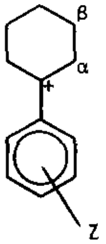
[a] The chemical shifts (δC) are in ppm downfield from tetramethylsilane. The chemical shifts of the amines are measured in $CDCl_3$ with internal tetramethylsilane. The chemical shifts of the protonated amines are measured in FSO_3H using 8-mm NMR tubes containing a concentric 3-mm (outside diameter) capillary tube of acetone-d_6 and tetramethylsilane. [b] All of the amines used here are commercially available. [c] Protonation shifts $\Delta\delta C = \Delta\delta C_{NH} - \Delta\delta C_{NH_2^+}$. The plus and minus signs mean the upfield and downfield protonation shifts, respectively.

The α-carbon atoms in these amines (1-5) undergo downfield (deshielding) shifts on protonation. This can be attributed to the inductive effect of the positive charge. Such downfield shifts were observed for the α-carbon atoms in arylcyclic carbocations with increasing the positive charge at the cationic carbon center.[1,2]

The β-carbon atoms in the amines (1-5) undergo upfield shift (shielding) on protonation. It has been suggested[4] that the cause for such a shift may be either a σ-inductive effect[3] or an electrostatic-field effect.[5] The σ-inductive effect has been suggested to alternate and attenuate along the carbon skeleton.[3] It is also suggested to be dependent on the conformation of the ring system.[3] The electrostatic-field effect has been suggested to operate through space and depend on the electric field of the positive charge, distance between the positive charge and the ^{13}C site and orbital orientations.[5] Although differentiation of these two effects is difficult, the observed results indicate that the upfield shift is highly dependent on conformation. In a relatively planar ring system, such as the pyrrolidine (2) system, the upfield shift is relatively small compared to the puckered (chair-boat) piperidine (3) system. The relatively larger protonation upfield shift observed for the β-carbon atom in azetidine (1) system might indicate the puckered nature of the ring system. The upfield shift observed for the β-carbon atom in hexamethyleneimine (4) is comparable to that observed for the piperidine (3) system. A similar upfield shift is observed for the quinuclidine (5) system.

The σ-inductive effect of the positive charge in protonated amines would be expected to fall off sharply as the distance between the positive charge and the ^{13}C site increases. However, the electrostatic-field effect could still be effective if the positive charge and the ^{13}C site could come closer in space because of conformational characteristics. Indeed, the magnitude of the upfield shift (+3.0) observed for the γ-carbon atom in the piperidine system (3) is comparable to that observed for the β-carbon atom. Accordingly, it appears that the electrostatic-field effect contributes more to the observed upfield shifts.

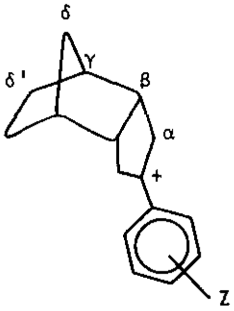
It is of interest to note that the $\underline{sp}^2$ hybridized positive charge in carbocations causes downfield shift compared to the upfield shift induced by the $\underline{sp}^3$ hybridized charge in protonated amines. For example, increasing the positive charge at the C^+ center in 1-aryl-1-cyclohexyl carbocations (p-OCH_3 to p-CF_3) causes downfield shift at the β-carbon atom by 11.3 ppm.[1] This is attributed to the hyperconjugative interaction of the β-carbon orbitals with the C^+ center.[1]



6

Z = p-OCH_3, δC_β = 35.4

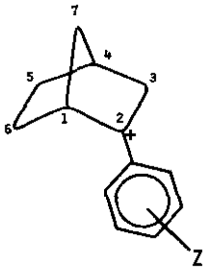
Z = p-CF_3, δC_β = 46.7



7

Z = p-OCH_3, δC_δ = 39.8

Z = p-CF_3, δC_δ = 38.3



8

Z = p-OCH_3, δC_5 = 26.5

Z = p-CF_3, δC_5 = 25.5

The inductive and hyperconjugative interactions between the C^+ center and the remote ^{13}C site in carbocations would fall off sharply as the distance between the two sites increases. Consequently, one would expect the C^+ center to cause upfield shift for certain remote ^{13}C sites similar to the effect observed for protonated amines. Indeed, at least in two cases (7 and 8), such upfield shifts are observed.[2,6] Since the inductive and hyperconjugative effects generally cause downfield shifts for the $\underline{sp}^2$ hybridized carbocations, the upfield shifts observed with increasing positive charge at the C^+ center in systems 7 and 8 appear to be due to the electrostatic-field effect of the positive charge. Consequently, these observations substantiate the conclusion that the upfield shifts observed for β- and γ-carbon atoms in protonated amines (1-5) are primarily due to the electrostatic-field effect of the positive charge on these carbon atoms.

ACKNOWLEDGEMENT - The author is grateful to Professor H. C. Brown for introducing him to the ^{13}C NMR field. This work was supported by a grant from Exxon Research and Engineering Company to Professor H. C. Brown.

REFERENCES

1. H. C. Brown and M. Periasamy, *J. Org. Chem.* 1981, 46, 3161.
2. H. C. Brown and M. Periasamy, *J. Org. Chem.* 1981, 46, 3166.
3. I. Morishima, K. Yoshikawa, K. Okada, T. Yonezawa and K. Goto, *J. Am. Chem. Soc.* 1973, 95, 165.
4. E. L. Eliel, W. F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dalling, M. W. Duch, E. Wenkert, F. M. Schell and D. W. Cochran, *J. Am. Chem. Soc.* 1975, 97, 322.
5. J. G. Batchelor, *J. Am. Chem. Soc.* 1975, 97, 3410.
6. H. C. Brown, M. Periasamy, D. P. Kelly and J. J. Giansiracusa, *J. Am. Chem. Soc.* submitted.

Received, 29th September, 1981