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References and Notes

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Steric and Electronic Effects on ^{15}N Chemical Shifts of Saturated Aliphatic Amines and Their Hydrochlorides¹

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Abstract: Natural-abundance ^{15}N NMR chemical shifts of saturated aliphatic primary, secondary, and tertiary amines and their hydrochlorides have been measured in different solvents. Good linear correlations of these ^{15}N shifts with the ^{13}C shifts of carbons in the same positions in the corresponding hydrocarbon analogues were only found for the primary compounds. The degree of correlation between ^{15}N and ^{13}C shifts decreased successively with secondary to tertiary amines and their hydrochlorides. Despite this, sets of solvent-dependent additive shift parameters were derived which give reasonably satisfactory agreement between calculated and experimental shifts of all of the amines and hydrochlorides. Some of the substituent-induced shifts appear to be conformational effects and can be compared with substituent effects observed previously for cyclic amines. The generally downfield protonation shifts could also be correlated with empirical substituent parameters.

I. Introduction

In previous reports on the natural-abundance ^{15}N spectra of saturated amines, it was shown that the nitrogen chemical shifts of primary and secondary amines could be correlated with a set of additive substituent-effect parameters.² Also, it was found that for a variety of saturated acyclic compounds the ^{13}C chemical shifts of a particular carbon could be correlated with the ^{15}N shifts of primary and secondary amines of corresponding structures where nitrogen replaces the particular carbon.^{2a}

More recently, the ^{15}N chemical shifts of methyl-substituted secondary and tertiary piperidines^{3a} and their hydrochlorides^{3b} were shown to be well described by substituent-shift parameters which have a close parallel to the parameters derived for calculation of ^{13}C chemical shifts of methylcyclohexanes.⁴ Separate linear ^{15}N -shift correlations with the ^{13}C shifts of the hydrocarbon analogues were demonstrated for the secondary and the tertiary piperidines and some related compounds. The tertiary amines were different from the secondary amines in being split into a minor and a major group having different $^{15}\text{N}/^{13}\text{C}$ correlation lines. There were also some tertiary amines which showed large deviations from either correlation line. The discrepancies were related to a stereoelectronic shift effect associated with having the lone pair on nitrogen anti-periplanar with respect to one or more carbon-hydrogen bonds

on the α carbons. Protonation was found to cancel this stereoelectronic effect and resulted in a change of the slopes of the $^{15}\text{N}/^{13}\text{C}$ shift-correlation lines from 1.9 (for the free amines in cyclohexane) to 1.1 (for the hydrochlorides in chloroform) and 1.4 (for the hydrochlorides in methanol). Furthermore, protonation diminished the upfield displacement of the correlation line of the tertiary amines from the correlation line for secondary amines from 12.5 ppm (free amines in cyclohexane) to 3.5 ppm (hydrochlorides in methanol). Most secondary and all tertiary piperidine hydrochlorides had downfield protonation shifts in methanol. The ^{15}N chemical shifts of tertiary amine hydrochlorides with gauche γ -carbon substituents as well as pyrrolidine and *N*-methylpyrrolidine hydrochlorides showed substantial deviations from the $^{15}\text{N}/^{13}\text{C}$ shift-correlation lines.

In the present research, the studies of shift correlations of natural-abundance ^{15}N NMR of saturated cyclic amines have been further extended to aliphatic primary, secondary, and tertiary amines. A priori, one might expect results similar to those for the cyclic amines, especially because quite useful ^{13}C substituent-effect parameters have been developed for aliphatic hydrocarbons.⁵ The principal difficulty to be expected lies in the fact that the conformational equilibria of saturated amines are different from those of the analogous hydrocarbons. Thus, the preferred conformation of propylamine around the C1-C2 bond is gauche, while for butane, the anti conformation is fa-

Table I. ^{15}N Shifts of Aliphatic Amines in Cyclohexane and Methanol, and Their Hydrochlorides in Methanol

Amine		$\delta^{15}\text{N}^a$			$\Delta\delta$ prot CH ₃ OH	$\delta^{13}\text{C}^b$
		Free bases C ₆ H ₁₂	CH ₃ OH	Hydrochloride CH ₃ OH		
Primary						
Methyl	1		371.1 ^c	355.2	-15.9	4.1
Ethyl	2	348.9 ^c	349.2 ^c	340.5	-8.7	15.5
Propyl	3	354.5	353.4	342.8	-10.6	13.1
Isopropyl	4	331.0	331.9	327.8	-4.1	24.2
Butyl	5	354.2	353.2	342.6	-10.6	13.5
<i>sec</i> -Butyl	6	336.2	336.0	329.7	-6.3	21.9
Isobutyl	7	358.0	356.5	344.9	-11.6	11.5
<i>tert</i> -Butyl	8	316.2	318.1	317.5	-0.6	31.6
Isoamyl	9	354.0	353.1	342.5	-10.6	14.3
Neopentyl	10	362.5	361.4	347.8	-13.6	8.5
<i>tert</i> -Amyl	11	322.2	322.4	319.0	-3.4	28.7
Cyclohexyl	12	334.6	334.2	329.5	-5.1	22.8
<i>trans</i> -4- <i>tert</i> -Butylcyclohexyl	13	334.6	334.8	329.5	-5.3	22.7
<i>cis</i> -4- <i>tert</i> -Butylcyclohexyl	14	343.4	343.5	335.4	-8.1	17.5
2-Adamantyl	15	340.3	340.3	333.3	-7.0	
1-Adamantyl	16	316.3	317.5	317.1	-0.4	31.5
Phenyl	17	320.8	322.3	326.4	+4.1	21.3
Secondary						
Dimethyl	18	364.9 ^c	363.3 ^c	350.4	-12.9	16.0
Ethylmethyl	19	346.6	345.8	337.5	-8.3	24.9
Diethyl	20	326.8	327.5	323.9	-3.6	34.1
Dipropyl	21	336.0	334.3	327.6	-6.7	29.0
Diisopropyl	22	298.9	300.3	303.8	+3.5	49.0
Dibutyl	23	335.5	333.8	327.3	-6.5	29.6
Diisobutyl	24	340.2	339.1	331.6	-7.5	25.2
Tertiary						
Trimethyl	25	360.7 ^c	356.9 ^c	343.2	-13.4	25.1
Ethyl dimethyl	26	349.0	345.1	333.8	-11.3	29.9
Diethylmethyl	27	336.9	334.3	324.9	-9.4	36.8
Triethyl	28	327.4	325.8	316.6	-9.2	42.4
Propyl dimethyl	29	352.2	346.6	334.7	-11.9	27.9
Isopropyl dimethyl	30	346.8	341.3	327.5	-13.8	34.0
Butyl dimethyl	31	352.2	346.6	334.7	-11.9	28.1
<i>sec</i> -Butyl dimethyl	32	352.7	343.4	327.4	-16.0	31.9
Isobutyl dimethyl	33	352.8	348.6	336.1	-12.5	25.7
<i>tert</i> -Butyl dimethyl	34	342.6	336.3	320.3	-16.0	37.9
Isoamyl dimethyl	35	352.2	346.7	334.6	-12.1	28.4
Neopentyl dimethyl	36	358.7		337.3		25.3
<i>tert</i> -Amyl dimethyl	37	348.4	338.7	320.5	-18.2	35.1
Dipropylmethyl	38	343.8	337.6	326.1	-11.5	32.3
Diisopropylmethyl	39	330.3	324.1	310.8	-13.3	45.3
Dibutylmethyl	40	343.5	337.4	326.2	-11.2	32.5 ^d
Diisobutylmethyl	41	344.5	343.2	328.9	-14.3	28.4 ^d
Cyclohexyl dimethyl	42	347.7	341.5	327.4	-14.1	
<i>trans</i> -4- <i>tert</i> -Butylcyclohexyl dimethyl	43	347.5		327.8		
1-Adamantyl dimethyl	44	342.7		319.8		
<i>N,N</i> -Dimethylphenyl	45	333.5	331.8	324.2	-7.6	34.1

^a Upfield from external HNO₃ (1 M). ^b Carbon-13 shift of the carbon in the structurally analogous hydrocarbon corresponding to the position of the nitrogen in the amine. Shifts downfield from Me₄Si, taken from ref 5 and 8. ^c Taken at 0–5 °C. ^d Carbon-13 shift calculated with the aid of the additive parameters of ref 5b.

vored.⁶ Because ^{15}N and ^{13}C shift effects depend on the orientations of substituents,³ this could well lead to poor correlations between ^{15}N and ^{13}C shifts.

II. Experimental Section

Nitrogen-15 chemical shifts were measured with a Bruker WH-180 FT NMR spectrometer operating at 18.25 MHz. The concentrations of the free amine solutions were 20 mol % in cyclohexane and 8 mol % in methanol (about 2 M). The spectra of the salts were taken as 4 mol % solutions in methanol (about 1 M). Continuous proton noise decoupling was employed at a power of 4–5 W, and to keep the sample temperatures at 20–30 °C, nitrogen at 0 °C was passed through the probe. The shifts were measured and are reported in parts per million upfield from external 1 M ^{15}N nitric acid in D₂O. The shift values which are reproducible to ca. 0.2 ppm have not been corrected for

bulk-susceptibility effects. The bulk susceptibility of the nitric acid reference is $-0.715 \pm 0.005 \times 10^{-6}$, the shift from external neat nitromethane is 6.2 ppm upfield, from external urea (2 M in H₂O) 298.7 ppm downfield, from external tetramethylammonium chloride (2 M in H₂O) 332.8 ppm downfield, and from the ammonium resonance of ammonium nitrate (2 M in H₂O) 355.0 ppm downfield. Reasonable signal-to-noise ratios were usually obtained on accumulation of 500–1000 pulses (25°/20 μs) using repetition rates of 2–5 s for primary amines, secondary amines, and all of the hydrochlorides. The repetition rates were 10–30 s for the tertiary amines.

The primary and secondary amines of this study were commercially available compounds. Liquid amines were freshly distilled from calcium hydride; solids were sublimed before measurement. Conversion of primary and secondary amines to *N*-methylated tertiary amines was achieved by the Leuckart method.⁷ The crystalline hydrochlorides were prepared by passing dry hydrogen chloride into solutions of the

Table II. Slopes, Intercepts, and Correlation Coefficients for Linear $^{15}\text{N}/^{13}\text{C}$ Shift Correlation

Compds	Solvent	Slope ^a	Intercept ^b	Correlation (r)	No. of examples
Primary amines	C ₆ H ₁₂	2.063	381.33	0.9982	14
Secondary amines	C ₆ H ₁₂	1.961	393.76	0.9941	7
Tertiary amines	C ₆ H ₁₂	1.387	391.4	0.9063	17
Primary amines	CH ₃ OH	1.951	379.02	0.9988	15
Secondary amines	CH ₃ OH	1.861	390.12	0.9915	7
Tertiary amines	CH ₃ OH	1.377	385.70	0.9531	16
Primary hydrochlorides	CH ₃ OH	1.402	361.06	0.9969	15
Secondary hydrochlorides	CH ₃ OH	1.383	370.11	0.9888	7
Tertiary hydrochlorides	CH ₃ OH	1.360	372.27	0.9523	16

^a The signs of the shifts were taken to obtain positive slopes. ^b Intercept on ^{15}N shift axis (positive values for upfield shifts).

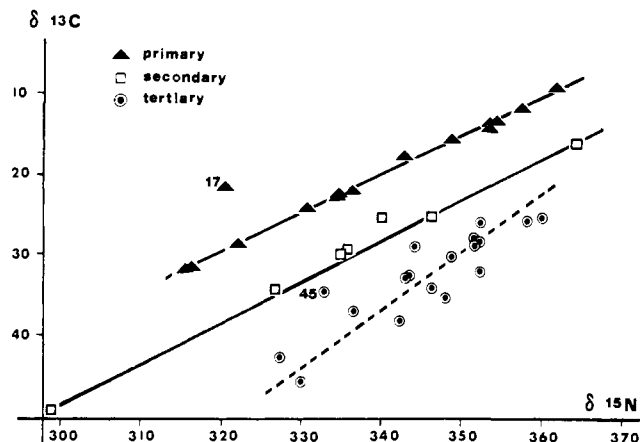


Figure 1. $^{15}\text{N}/^{13}\text{C}$ shift correlation for aliphatic amines in cyclohexane as solvent. The slopes of the correlation lines correspond to those in Table I. All points included, except those for 17 and 45.

free amines in anhydrous ether. The salts were collected by filtration, washed with ether, and dried under reduced pressure.

III. Results and Discussion

The ^{15}N chemical shifts of various saturated aliphatic primary, secondary, and tertiary amines in cyclohexane and methanol solution as well as the shifts of their hydrochlorides dissolved in methanol are listed in Table I together with the protonation shifts and the ^{13}C chemical shifts of the corresponding carbons in the related hydrocarbons. The carbon shifts were either obtained from the literature^{5,8} or calculated using the additive parameters determined by Lindeman and Adams.^{5b} Plots of the nitrogen vs. carbon shifts are shown in Figure 1 for the free amines in cyclohexane, in Figure 2 for the free amines in methanol, and in Figure 3 for the hydrochlorides in methanol. In all three plots, the points corresponding to the secondary compounds are displaced upfield (on the nitrogen scale) from the primary compounds, and the tertiary shift pairs upfield from the secondary ones. As shown previously,^{2a} ^{15}N shifts of primary amines,⁵ except for aniline (17), give a very good linear correlation with the appropriate ^{13}C shifts of the corresponding methyl groups in hydrocarbons. We now find a similarly good fit for the hydrochlorides of primary amines. A rather reasonable linear correlation was also observed for the secondary compounds, but a number of compounds show substantial deviations, especially the hydrochlorides. Matters are much worse for the tertiary amines and their hydrochlorides, and this contrasts with the behavior of methyl-substituted *N*-methylpiperidines and their hydrochlorides where good linear correlations were found which included many substances with nitrogen shifts covering about the same range as those encountered in this study.³ The degree of success of the linear $^{15}\text{N}/^{13}\text{C}$ relationships is more evident from Table II, where

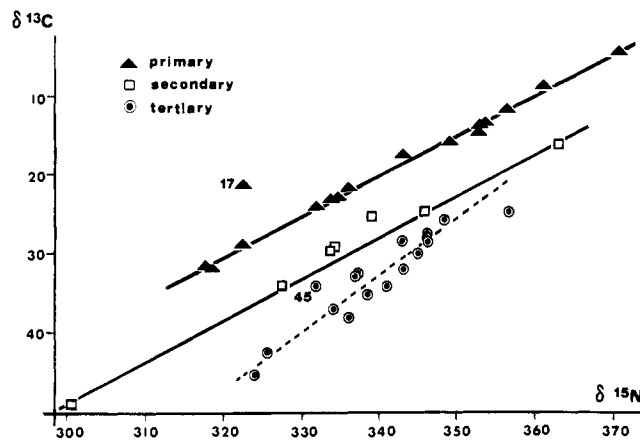


Figure 2. $^{15}\text{N}/^{13}\text{C}$ shift correlation for aliphatic amines in methanol as solvent. The slopes of the correlation lines correspond to Table I. All points included, except those for 17 and 45.

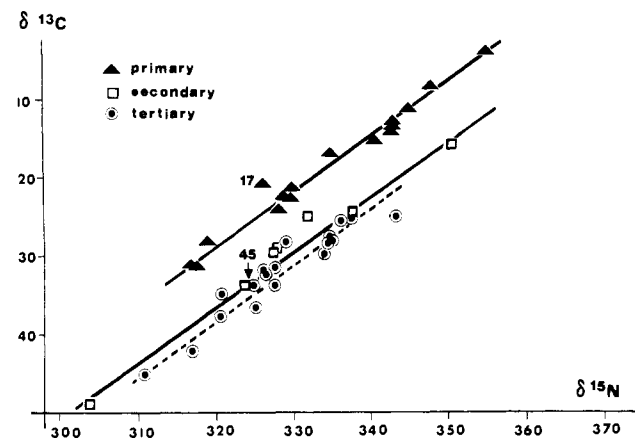


Figure 3. $^{15}\text{N}/^{13}\text{C}$ shift correlation for aliphatic amine hydrochlorides in methanol. The slopes of the correlation lines correspond to Table I. All points included, except those for 17 and 45.

the slopes, intercepts and correlation coefficients of the least-squares lines are listed. The shifts of aniline (17) and *N,N*-dimethylaniline (45) were excluded from the least-squares error analysis.

Figures 1–3 show that going to a more polar and hydrogen-bonding solvent, or protonating the amines, tends to bring $^{15}\text{N}/^{13}\text{C}$ shift-correlation lines closer together. The changes are smaller for primary and secondary amines than for secondary and tertiary amines. Thus, the separation between the correlation lines for the primary and secondary amines for a carbon shift of 30 ppm is 16.8 ppm for cyclohexane as solvent, 15.7 ppm for methanol as solvent, and 11.3 ppm for the hydrochlorides. The corresponding figures for secondary and tertiary amines are 12.5 to 8.7 to 3.5 ppm.

Table III. Deviations of ^{15}N Chemical Shifts of Amines and Amine Hydrochlorides from the $^{15}\text{N}/^{13}\text{C}$ Correlation Line^a

		Amines		Hydrochlorides
		C_6H_{12}	CH_3OH	CH_3OH
		Primary		
Phenyl	17	16.6	15.2	4.8
		Secondary ^b		
Dimethyl	18	0.5	0.4	0.3
Ethylmethyl	19	0.1	-0.1	0.0
Diethyl	20	-1.3	-0.8	-0.6
Dipropyl	21	2.3	3.8	4.1
Diisopropyl	22	0.7	0.5	0.4
Dibutyl	23	1.6	3.1	3.6
Diisobutyl	24	5.7	6.2	5.5
		Tertiary ^c		
Trimethyl	25	-1.2	-1.5	-0.9
Ethylmethyl	26	1.4	1.9	-1.3
Diethylmethyl	27	-0.4	-0.5	-0.2
Triethyl	28	-0.7	-0.9	-0.3
Propyldimethyl	29	2.0	3.5	3.4
Isopropyldimethyl	30	-4.2	-1.6	1.4
Butyldimethyl	31	1.6	3.5	3.1
<i>see</i> -Butyldimethyl	32	-6.1	0.0	4.7
Isobutyldimethyl	33	5.6	5.7	5.3
<i>tert</i> -Butyldimethyl	34	-7.4	-3.4	2.8
Isoamyldimethyl	35	-1.1	2.9	2.8
Neopentyldimethyl	36	-0.5		4.7
<i>tert</i> -Amyldimethyl	37	-7.8	-0.9	6.8
Dipropylmethyl	38	2.1	5.1	5.4
Diisopropylmethyl	39	-9.1	-4.3	1.2
Dibutylmethyl	40	2.0	5.0	5.0
Diisobutylmethyl	41	8.8	6.4	8.5
<i>N,N</i> -Dimethyl-phenyl	45	9.0	7.8	4.6

^a Deviation on nitrogen-shift scale: δ calculated (from slope and intercept) - δ experimental. ^b The deviations given for the secondary amines are from the correlation line calculated for the shifts of **18**, **19**, **20**, and **22** (see text). ^c The deviations given for the tertiary amines are from the correlation line calculated for the points for **25-28** alone (see text).

The $^{15}\text{N}/^{13}\text{C}$ shift correlations are clearly excellent for primary amines in different media as either the free bases or the salts. The slope and intercept for these amines compare well with the values determined earlier (2.05 and 380.2, respectively, for the neat amines).^{2a} The 17-ppm deviation of the shift of aniline (**17**) from the correlation line has been ascribed to conjugative interactions of the lone pair with the aromatic ring. This is in accord with the fact that the deviation becomes smaller in methanol and drops to 5 ppm for the hydrochloride (Table III). *N,N*-Dimethylaniline (**45**) behaves similarly.

The correlation for secondary amines is not as good as for primary amines. Most of this seems to be associated with the presence of γ carbons, as for dipropylamine (**21**), dibutylamine (**23**), and diisobutylamine (**24**), and if these amines are omitted, the least-squares correlation r becomes 0.995, the slope 2.005, and the intercept 396.5. The predicted shifts of these amines are all *downfield* of the experimental values, and the deviations increase with the number of γ carbons, with the solvent polarity, and on protonation (Table III). The slope of the secondary amine correlation line, excluding **21**, **23**, and **24**, is nearly parallel to that for all of the primary amines and only slightly different for that observed for piperidines.^{3a} The slope (1.67) previously determined for $^{15}\text{N}/^{13}\text{C}$ shift correlations of secondary amines^{2a} largely involved azacycloalkanes with different ring sizes, and because the effects of angle strain on nitrogen chemical shifts have not yet been elucidated, it is probably not surprising that a different slope was obtained. The important point with secondary amines is that their experi-

mental shifts, when γ carbons are present, are uniformly downfield of what is expected from the ^{13}C shifts of the corresponding hydrocarbons. Because nonbonded interactions usually produce upfield ^{13}C shift changes, it seems necessary to conclude that *acyclic* amines have an added degree of flexibility through bond-angle or conformational changes so as to minimize the effect on nonbonded interactions on their ^{15}N shifts.

Tertiary amines give rather wide scatter from the correlation line and the average slope for either solvent (about 1.4) for all of the samples studied is substantially smaller than the slopes for primary or secondary amines (1.9-2.1). If we take only the four tertiary amines (**25-28**) with no branching and no γ carbons, we find that over a 30-ppm spread of ^{15}N shifts in cyclohexane solutions, there is a $^{15}\text{N}/^{13}\text{C}$ correlation coefficient of 0.9935, a slope of 1.8971, and an intercept of 407.1 ppm. These values are not very different from those found for secondary amines in cyclohexane. If we assume that the shifts of these unbranched amines and their hydrochlorides are "normal", then we might expect that the pattern of differences between calculated and experimental shifts of the other amines and their hydrochlorides, as listed in Table III, could give clues as to why the tertiary amines, on the whole, are poorly correlated.

Even a glance at Table III shows some significant trends. Thus, the deviations of the tertiary amine hydrochlorides of **29-41** are like those of the secondary amine hydrochlorides, **21**, **23**, and **24**, in corresponding to predictions of resonance lines farther *downfield* than actually observed. However, the free amines, **29-41**, show a welter of positive and negative deviations which speak for some rather large upfield shift influence(s) characteristic of the amine but not of the hydrochlorides. The obvious shift effects expected for the amines but not the hydrochlorides are unshared pairs of the amino nitrogens.

The deviations observed for the experimental shifts of tertiary amines from the calculated values have a parallel with the deviations observed for *N*-methylpiperidines.³ One effect has been ascribed to hyperconjugation of the unshared pair with the hydrogens on the α carbons and is expected to be canceled either by protonation or by substitution of alkyl groups for the particular α hydrogens involved. This sort of influence is evident through the upfield deviations from the correlation line for the tertiary amines. The deviations for these amines are smaller in methanol than in cyclohexane and disappear on protonation. On the other hand, increasing downfield deviations are observed for tertiary amines with γ carbons, such as isobutyldimethylamine (**33**) and diisobutylmethylamine (**41**), that have counterparts with secondary aliphatic amines, as described above, and *N*-methylpiperidines carrying axial γ -methyl groups.³ For the latter kind of compound, the shift effects have been accounted for by postulating a change in the conformational equilibrium involving the lone pair. The deviations with amines such as **33** and **41** are not removed by protonation, which is consistent with what has been found for tertiary *N*-methylpiperidine hydrochlorides with *gauche* γ -methyl groups.^{3b} With those tertiary aliphatic amines that have *both* branched α carbons and γ substituents (e.g., *sec*-butyldimethyl- and *tert*-amyldimethylamines, **32** and **37**), the branching effect dominates the ^{15}N chemical shifts of the free bases, producing upfield deviations. However, for the hydrochlorides of these amines, the typical downfield deviations of tertiary amines with γ carbons are found.

The slopes of the $^{15}\text{N}/^{13}\text{C}$ shift correlations of primary, secondary, and tertiary amine hydrochlorides as 4 mol % solutions in methanol at ambient temperatures are all close to 1.4. Differences between aliphatic and cyclic hydrochlorides can be seen to be less pronounced than for the amines, and, in general, the structural influences on the ^{15}N chemical shifts

Table IV. Additive Substituent-Effect Parameters

Parameter ^a	Free bases		Hydrochlorides CH_3OH^b	$\Delta\delta$ protonation (CH_3OH) CH_3OH^b
	$\text{C}_6\text{H}_{12}^b$	CH_3OH^b		
B^p	372.6 (1.6/10)	371.0 (0.7/11)	355.6 (0.4/11)	-15.3 (0.4/11)
B^s	365.1 (1.3/7)	363.6 (0.8/7)	350.4 (0.4/7)	-12.8 (0.3/23)
B^t	361.5 (0.9/17)	355.9 (0.6/16)	343.0 (0.3/17)	
β^p	-22.6 (1.4/10)	-21.3 (0.8/10)	-15.2 (0.4/10)	+5.8 (0.4/10)
β^s	-19.0 (0.8/6)	-18.3 (0.5/6)	-13.5 (0.3/6)	+4.5 (0.2/6)
β^t	-11.7 (0.5/16)	-10.5 (0.4/15)	-9.1 (0.2/16)	+1.5 (0.2/15)
$\gamma^{p,s}$	3.8 (0.4/10)	3.4 (0.3/10)	2.2 (0.1/10)	
γ^t	2.2 (0.3/10)	1.8 (0.2/9)	0.9 (0.1/10)	-1.1 (0.1/19)
Cor $\beta^{p,s}$	4.9 (1.4/5)	5.0 (0.9/5)	3.6 (0.5/5)	-1.0 (0.4/5)
Cor β^t	8.2 (0.7/5)	5.7 (0.5/5)	2.2 (0.3/5)	-3.7 (0.3/5)
Cor $\gamma^{p,s,t}$	1.8 (0.6/4)	0.6 (0.4/4)	-0.4 (0.2/4)	-1.0 (0.3/4)
Corr coeff	0.9967 (34) ^c	0.9984 (34) ^c	0.9992 (35) ^c	0.9937 (34) ^c
Std dev	1.38	0.96	0.52	0.60

^a p, s, t stand for primary, secondary, and tertiary. ^b Parenthetical values are the deviation and number of occurrences for each parameter. ^c Total numbers of compounds considered are in parentheses.

Table V. ^{15}N Chemical Shift Effects (ppm) Produced by γ Methyl Group Substitution on Some Aliphatic Amines^a

Solvent				
		C_6H_{12}	CH_3OH	HCl, CH_3OH
Primary, R = H	5.6	3.5	4.5	
Tertiary, R = CH_3	C_6H_{12}	4.2	3.1	4.9
	CH_3OH	2.8	2.1	2.9
	HCl, CH_3OH	3.2	0.6	5.9
	C_6H_{12}	1.5	2.0	
	HCl, CH_3OH	0.9	1.4	1.2
	C_6H_{12}	5.6	5.2	6.0
Primary, R = H	CH_3OH	4.2	4.1	4.3
	HCl, CH_3OH	2.8	1.9	1.5
	C_6H_{12}	3.2	5.9	5.8
Tertiary, R = CH_3	CH_3OH	1.5	2.1	2.4
	HCl, CH_3OH	0.9	0.1	0.2
		C_6H_{12}	9.2	4.2
Secondary, R = H	CH_3OH	6.8	4.8	
	HCl, CH_3OH	3.7	4.0	
	C_6H_{12}	6.9	0.7	
Tertiary, R = CH_3	CH_3OH	3.3	5.6	
	HCl, CH_3OH	1.2	2.8	

^a Shift effects observed for the encircled γ -methyl group.

of the amine salts are more similar to the ^{13}C shifts of hydrocarbons than for the amines.

Table IV contains sets of additive substituent-effect parameters found by multilinear regression analysis for the ^{15}N chemical shifts of the free amines in both cyclohexane and methanol, of the corresponding hydrochlorides in methanol, and also for the shift changes occurring on protonation, for use in the following relation:

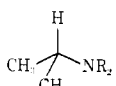
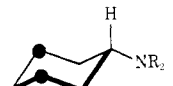

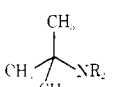
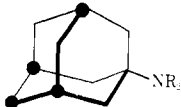
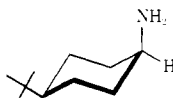
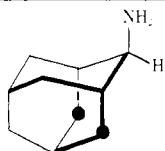
$$\delta^i = B^i + a_1\beta^i + a_2\gamma^i + a_3(\text{cor } \beta^i + \text{cor } \gamma^i)$$

where i refers to whether the parameter set corresponds to primary, secondary, or tertiary amine or salt; B^i , base values; β^i , γ^i , parameters for each carbon two and three bonds from nitrogen, respectively; cor β^i , correction for branching at $\text{C}(\alpha)$;

cor γ^i , additional correction for branching at $\text{C}(\alpha)$ if there is a γ carbon at the same residue; a_1, a_2, a_3 , number of β carbons, γ carbons, and branches on α carbons, respectively. The way the parameters are used can be illustrated with *tert*-amyldimethylamine in CH_3OH , $\delta^t = B^t + 3\beta^t + \gamma^t + 2(\text{cor } \beta^t + \text{cor } \gamma^t) = 355.9 + 3(-10.5) + 1.8 + 2(5.7 + 0.6) = 338.8$ ppm, which is to be compared with the experimental value of 338.6 ppm.

The parameters in Table IV are rather different from the parameters determined previously using a much smaller data set without considering branching effects.² A few of the parameters are about the same for primary, secondary, and tertiary aliphatic amines. In general, 11 parameters suffice for the amine shifts and nine for the protonation shifts. As be-

Table VI. ^{15}N Chemical Shifts of Amines with and without Anti γ Carbons (ppm from HNO_3)

				
Primary R = H	C_6H_{12}	331.0	334.6	334.6
	CH_3OH	331.9	334.2	334.8
	HCl, CH_3OH	327.8	329.1	329.5
Tertiary R = CH_3	C_6H_{12}	346.6	347.7	347.5
	CH_3OH	341.3	341.5	
	HCl, CH_3OH	327.5	327.4	327.8
				
Primary R = H	C_6H_{12}	316.2	316.3	
	CH_3OH	318.1	317.5	
	HCl, CH_3OH	317.5	317.1	
Tertiary R = CH_3	C_6H_{12}	342.6	342.7	
	CH_3OH	336.3		
	HCl, CH_3OH	320.3	319.8	
				
Primary	C_6H_{12}	343.4	340.3	
	CH_3OH	343.5	340.3	
	HCl, CH_3OH	335.4	333.3	

fore,^{2b,3} it was found that δ substituents have no significant influence on the ^{15}N chemical shifts of saturated amines.

The β substitution effects are the largest and are decreased by N-alkylation, by hydrogen bonding to the lone pair, or by protonation. The "cor β " parameter corresponds to a diminishing of the β effect through branching on C(α). This parameter is especially large for tertiary free amines in cyclohexane.

The shift effects produced by γ substitutions are complicated. The small to intermediate upfield shifts found for cyclohexane solutions decrease in methanol or on protonation and are smaller for tertiary amines than for secondary or primary amines. An important influence here is probably connected with conformational changes that change the stereoelectronic relationships of the C-C bonds and the lone pair. Table V lists the shift effects produced by γ -methyl groups for individual amines. The shift changes are intermediate between the effects found for equatorial (anti) and axial (gauche) methyl groups of piperidines.³ Because propylamine prefers the gauche conformation, methylation of a β carbon of an *N*-ethyl group should have a larger upfield ^{15}N -shift effect on the nitrogen for the first methyl and the third methyl than for the second methyl group. This pattern of shift changes is indeed observed for ethyldimethylamine (**26**) and diethylmethylamine (**27**), and to a lesser extent for ethyl- and diethylamine (**2**, **20**) (Table V). The data of Table V also indicate that the preference for the conformation with gauche propyl groups decreases in a strongly hydrogen-bonding solvent (methanol) or on protonation.

The population of amine conformations with gauche γ groups should be made more favorable than for simple propyl groups by branching on the α carbon. Such population changes have analogies in the conformational preferences of *cis*-decahydroquinoline⁹ and *cis*-2,3-dimethylpiperidine.^{3,10} On this basis, larger upfield shifts are expected and found to be associated with the γ carbons of *sec*-butyl and *tert*-amyl than for propyl substituents (see Table V). The "cor γ " parameter

has been introduced to quantify the shift effects connected with this sort of conformational change. The parameter is not far from the limit of statistical relevance but it does show the expected solvent dependence and sign change for salt formation.

The effects of anti γ carbons were studied with the aid of cyclic model compounds. The shifts obtained are summarized in Table VI. One important point is that whatever causes the changes of ^{13}C shifts produced by heteroatoms on anti γ carbons,^{11,12} it does not seem to operate in the same way on the ^{15}N chemical shifts of saturated amines. No shift effect at all was found for equatorial γ -methyl groups in piperidines.^{3a} The small upfield shift of cyclohexylamine relative to isopropylamine, and the small downfield shift of 2-aminoadamantane relative to *cis*-4-*tert*-butylcyclohexylamine, are slightly reduced, certainly not canceled, by protonation, and are therefore difficult to rationalize in terms of heteroatom effects. The three γ carbons of 1-aminoadamantane seem to have no influence on the shifts of the free amine or of the hydrochloride. Where ^{13}C chemical shifts of hydrocarbons analogous to the amines of Table VI were available, the same shift effects are observed (Table I). Therefore the effects of anti γ carbons on ^{15}N chemical shifts are not evident in $^{15}\text{N}/^{13}\text{C}$ shift correlations.

The protonation-shift parameters of Table IV show the same trends found for the piperidines.^{3b} The deshielding protonation effect is decreased by β substituents, more so for primary and secondary amines than for tertiary amines, but also increased by branching at the α carbons, especially for tertiary amines, and by γ carbons. The correlation coefficient of the least-squares analysis is smaller than for the shift calculations because the protonation shifts are differences between two experimental measurements.

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Amine Quenching of Aromatic Fluorescence and Fluorescent Exciplexes¹

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Abstract: Quenching of the fluorescence of naphthalene, a number of naphthalene derivatives, and fluorene by tertiary amines has been studied. In most cases fluorescent exciplexes are produced, although 1,4-diazabicyclo[2.2.2]octane (Dabco) quenches both naphthalene and fluorene very efficiently without producing any exciplex emission. Stern-Volmer constants for quenching, quantum yields and lifetimes for exciplex fluorescence, and shifts of exciplex emission with structural change and solvent properties have been measured. Most of the results can be rationalized qualitatively in terms of structures of the exciplexes involving extensive charge transfer from the amines to the aromatic fluors. Substituent effects on exciplex emission frequencies have been analyzed semiquantitatively as have solvent effects on emission frequencies. Both approaches indicate that the ionic character of the exciplexes is high, but less than 100%. Shifts in emission frequency are well correlated as a function of dielectric constant and polarizability for most solvents, although unexpectedly large red shifts are observed in 1,4-dioxane, benzene, and toluene. In the case of dioxane the anomaly is attributed to submolecular dipole-dipole interaction, and, in the case of the aromatic solvent, to the fact that internal pressures are higher than for aliphatic solvents. The data for mixed solvents consisting of cyclohexane with dioxane or tetrahydrofuran indicate preferential solvation of the exciplexes by the ethers.

There are many reported examples of the quenching of fluorescence of aromatic compounds by species which cannot function by simple transfer of electronic excitation energy because the quenchers do not have sufficiently low lying singlet excited states.²⁻²² Two situations are encountered. In some cases, principally exemplified by the quenching of aromatic hydrocarbons by amines,^{7-9,14-17} fluorescent exciplexes are formed and readily recognized by the appearance of broad, structureless emission shifted far to the red in comparison with the characteristic emission of the parent aromatic fluor. In other cases very efficient quenching occurs without the appearance of new emission. Familiar examples are quenching of the fluorescence of aromatic hydrocarbons by unsaturated hydrocarbons of rather simple structure.^{2,3,5}

The evidence that the fluorescent exciplexes formed from the excited singlet states of aromatic compounds and tertiary amines derive much of their binding energy from charge transfer interaction^{7-9,14} is supported by the large medium effects on the wavelengths of the exciplex emission and by the fact that in polar solvents dissociation to separated ion radicals occurs.^{9,14,18} A recent example has been reported in which donor and acceptor roles of quencher and quenchee are reversed.²⁰

Arguments based upon structure-reactivity relationships have been advanced to associate nearly all quenching without electronic energy transfer to charge-transfer interactions.¹⁰⁻¹²

This view has recently received added support by the observation that fluorescent exciplexes are formed from negatively substituted aromatic compounds and simple olefinic compounds.^{12,20} However, we have previously pointed out⁵ that there are large discontinuities in correlations of quenching reactivity with ionization potentials and electron affinities when series of compounds in different classes are compared.

In this paper we present the results of a kinetic study of quenching and exciplex emission in the interaction between naphthalenes and fluorene with triethylamine (TEA), *N*-methylpiperidine (NMP), and 1,4-diazabicyclo[2.2.2]octane (Dabco).

Results

In the absence of triethylamine the emission spectrum of naphthalene in cyclohexane shows two maxima at 325 and 344 nm with a shoulder at around 348 nm (Figure 1). In the presence of TEA, the intensity of the naphthalene fluorescence is reduced and simultaneously a new emission band, attributed to an exciplex, is observed. As is usually the case¹³ the exciplex emission is structureless and red-shifted from the naphthalene emission with a maximum at 410 nm (Figure 1). Initially, as the quencher concentration increases, the intensity of the 410-nm maximum increases at the expense of the naphthalene fluorescence. Further increase in the quencher concentration results in a reduced intensity of this emission also. At sufficiently high concentration of triethylamine, the naphthalene fluorescence is almost completely quenched and the new

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