Carbon-13 Nuclear Magnetic Resonance Spectra of Acyclic Aliphatic Amines

Hanne Eggert[1] and Carl Djerassi*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received October 26, 1972*

Abstract: Fourier transform C-13 nuclear magnetic resonance spectra have been obtained for 103 aliphatic amines. Correlation formulas capable of predicting unknown shifts are given. Conformational effects on the C-13 chemical shifts of γ carbon atoms are considered.

This paper describes the results of an investigation of the carbon-13 nuclear magnetic resonance (C-13 nmr) spectra of aliphatic amines, which was undertaken as an extension of our Artificial Intelligence program. Previous publications on this subject[2] have described the results of computer interpretations of mass spectra, in some cases with the aid of proton nmr data. These methods are very useful for the elucidation of the immediate environment around a functional group. However, evidence from mass spectra and proton nmr about portions of the molecule which are relatively remote from the functional group is usually not very specific, especially when dealing with compounds incorporating large hydrocarbon moieties. This limitation does not apply to evidence from C-13 nmr spectra. Furthermore, it has been found that the effects of substituents on C-13 chemical shifts are largely additive,[3,4] so predictions of C-13 chemical shifts on the basis of empirical correlations are usually successful. These facts indicate that C-13 nmr spectral data would be very suitable for computer assisted identification of unknown compounds.

In order to examine this further, we have investigated the C-13 nmr spectra of aliphatic amines. These were chosen because generally mass spectra of amines yield information which is limited to the degree of substitution at the carbon atoms next to the nitrogen atom. Likewise, proton nmr spectra of amines usually provide information primarily about the atoms closest to the nitrogen atom, and even a combination of mass spectra and proton nmr spectra is not always sufficient to give an unambiguous identification of an examined amine.[5] Unfortunately, only very few C-13 nmr data for amines are available. Therefore the objective of the present work was to collect sufficient data on C-13 chemical shifts for amines so as to establish a parameter set describing the C-13 nmr spectra of acyclic, aliphatic amines with an accuracy sufficient for the further use in computer interpretation of spectra of unknown amines.

Experimental Section

The Fourier transform (FT) C-13 nmr spectra were obtained using a Varian XL-100-15 spectrometer operating at 25.2 MHz, equipped for pulsed Fourier transformation. The instrument was controlled with a Varian 620-i computer. The Fourier transforms were based upon 2048 data points and employed the absorption spectrum. Field/frequency lock was established *via* the deuterium resonance of internal C_8D_6. Depending on sample concentration, averaging of between 500 and 2000 transients was used for completely proton decoupled spectra, and about four times as many for off-resonance decoupled spectra.

Spectra were obtained in C_6D_6 solution with internal TMS as standard in 12-mm sample tubes. Most samples were prepared as mixtures of 3 ml of amine with 0.5 ml of C_6D_6 and 0.5 ml of TMS. In cases where only very little amine was available C_6H_6 was added to give a total volume of 4 ml. The C-13 chemical shifts were found to be nearly independent of concentration. Probe temperature for all experiments was *ca.* 30°. Spectral reproducibility was ±0.04 ppm for the individual solutions.

The amines employed in this investigation were commercial samples or were prepared by standard methods and purified by distillation.

Results

The C-13 chemical shift data are presented in Tables I–III. α designates carbon atoms one bond away from the nitrogen atom, β carbon atoms two bonds away, γ three bonds away, and so on. The assignments of the individual chemical shifts have been made by consideration of the relative peak intensities and by taking advantage of the fact that carbon atoms in two different molecules which have the same environment within the nearest four carbon atoms have the same chemical shift within the experimental error. In aliphatic amines this means that carbon atoms at least five bonds away from the nitrogen atom should have nearly the same chemical shifts as the similar located atoms in the corresponding alkane, defined by replacement of the nitrogen atom with a CH group. The chemical shifts of the C atoms of alkanes can be calculated,[6] and the assignment of absorptions corresponding to carbon atoms more than five bonds away from the nitrogen is hence straightforward. The remaining peaks have been assigned by comparing spectra of compounds containing closely related structures and correlating the systematic shifts due to slight differences in structure, and by use of off-resonance decoupled spectra. Using these assignments additive substituent parameters are obtained, while other assignments would result in internal inconsistencies. In a

(1) Recipient of a fellowship from the American Association of University Women.

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(6) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).

few cases two resonances appear too close to each other to permit unequivocal assignment. In these cases the assignments giving the more favorable agreement were used. The possible errors introduced hereby will not cause significant changes in the parameters given.

Discussion

Brown[7] has reported substituent parameters for the NH_2 group, based on very limited number of experimental data; no parameters have been reported for secondary and tertiary amines. Roberts, *et al.*,[8] have shown that a simple linear correlation exists between the chemical shifts of carbon atoms in alcohols and the corresponding hydrocarbon wherein a methyl group replaces the oxygen function. In this paper we show that a similar correlation also exists for amines, and as a consequence it is possible to predict the chemical shifts of amines, since the shifts of the C atoms of alkanes can be calculated using the parameter set of Lindeman and Adams.[6] The standard deviation for the correlation of primary and secondary amines with alkanes is close to that for the correlation of experimental and calculated alkane chemical shifts (0.79 ppm), whereas the deviation is somewhat larger for the tertiary amines.

By the method of least-squares fit, set 1 of the equations summarized in Table IV was obtained for α, β, and γ carbon atoms in different types of amines. For the chemical shifts of δ carbon atoms and beyond the correlations were found to have $A = 1$ and $B = 0$ (see Table IV), within the standard deviation given for the alkane parameter set (0.79 ppm). The values for δ_C^{alkane} used in establishing the correlations were calculated in all cases,[6] even where experimental data were available in order not to make the use of the parameter set dependent on the availability of experimental data for alkanes. For primary amines a better fit than that given may be obtained if experimental alkane values are used instead of the calculated ones.

To correct for differences in chemical shift caused by the different solvents used in this work (benzene) and in the work of Lindeman and Adams[6] on alkanes (dioxane), 0.35 ppm was added to all calculated alkane chemical shifts. This value represents the average deviation of experimental alkane chemical shifts from the experimental amine values for all carbon atoms five or more bonds away from the nitrogen atom. One further correction was introduced into the alkane parameter set: the calculated chemical shift for a secondary carbon atom connected to two quaternary carbon atoms deviates 1.7 ppm from the experimental value and we have corrected for this by adding 1.70 ppm to the calculated value.

Examination of the correlations between amine and alkane chemical shifts revealed that the largest standard deviations usually were caused by a few branched structures. In these cases much better correlations are obtained by addition of constant terms to the calculated alkane values for certain branched substructures. These are summarized in Table V, and while a few terms are needed for primary and secondary amines, more are required with tertiary ones. This is not too surprising as branching at one or more of the α carbon atoms in tertiary amines results in quite crowded molecules, for which the alkane parameter set works less well. It remains to be seen whether these terms are peculiar to amines or whether they may also serve as extensions to the alkane parameter set.

The list of correctional terms summarized in Table V is not exhaustive, since the experimental material does not include all possible kinds of alkyl structures around the nitrogen atom, but it is believed to cover the more common cases. With these corrections applied to the calculated alkane chemical shifts, set 2 of the correlations summarized in Table IV is obtained.

For some purposes it is more useful to compare a primary amine with that hydrocarbon from which it is derived. Table VI contains the effects caused by replacement of a hydrogen atom in a hydrocarbon by an amino group. In this table experimental values have been used for the alkane chemical shifts. Brown has reported[7] the following substituent effects for the NH_2 group in alkanes: +29, +11.4, −4.6, and +0.6 ppm for α, β, γ, and δ carbon atoms, respectively. They were derived from the spectra of five straight-chain amines (methyl- through pentylamine) and they agree well with those found in this study for straight-chain primary amines. It appears from Table VI that fixed substituent parameters should be used only with caution for prediction of chemical shifts as substituent effects vary considerably and can only be considered to be constant for very similar structures.

A comparison of the correlations for primary, secondary, and tertiary amines shows that there are only small differences between these for α, β, and γ carbon atoms, and that if one accepts a somewhat larger standard deviation, they may be combined into one set of equations. In the work of Roberts, *et al.*,[8] on similar correlations for alcohols lines of unit slope were found for β and γ carbon atoms. It is possible that the deviation from unit slope found in our work is fortuitous, arising from the choice of compounds examined, but it is striking that it is in all cases less than one. The effect of an amino group on the α carbon atoms compared with that of a hydroxyl group[8] is much smaller (about 20 ppm), while the shifts introduced at β and γ carbon atoms relative to the corresponding alkane are about the same.

In general, an upfield shift is observed at the γ carbon atoms when a methyl group or a more polar substituent is introduced into a hydrocarbon. Studies on methylcyclohexanes[9,10] and norbornyl derivatives[11] have supported the original idea of Cheney and Grant[12] that the shielding effect on a γ carbon atom introduced by substitution is mainly caused by a 1–4 nonbonded steric interaction in the gauche rotamer. This substituent effect is usually found to be larger when the substituent is polar than when it is a methyl

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Table I. C-13 Chemical Shifts (ppm) in Primary Amines Relative to TMS

	Amine	α	β	γ	δ	ε	ζ	η	θ	ι	κ
C_1	Methylamine	28.3[a]									
C_2	Ethylamine	36.9	19.0[a]								
C_3	Propylamine	44.58	27.40	11.54							
	Isopropylamine	42.96	26.45								
C_4	Butylamine	42.33	36.75	20.47	14.16						
	sec-Butylamine	48.79	33.42 (C2) 23.97 (C2′)	10.81							
	Isobutylamine	50.62	32.05	20.20							
	tert-Butylamine	47.20	32.87								
C_5	Pentylamine	42.65	34.30	29.69	23.10	14.28					
	1-Methylbutylamine	46.85	42.78 (C2) 24.02 (C2′)	19.85	14.32						
	2-Methylbutylamine	48.36	38.50	27.20 (C3) 17.20 (C3′)	11.55						
	3-Methylbutylamine	40.58	43.71	25.89	22.89						
	2,2-Dimethylpropylamine	54.45	32.08	27.00							
C_6	Hexylamine	42.66	34.59	27.12	32.34	23.15	14.22				
	1,3-Dimethylbutylamine	44.71	50.15 (C2) 25.14 (C2′)	25.14	22.49 (C4) 23.37 (C4′)						
	1,2,2-Trimethylpropylamine	55.62	34.35 (C2) 18.71 (C2′)	25.97							
	2,2-Dimethylbutylamine	52.46	34.63	31.84 (C3) 24.32 (C3′)	8.36						
C_7	Heptylamine	42.53	34.45	27.36	29.71	32.37	23.05	14.20			
	1-Methylhexylamine	47.14	40.81 (C2) 24.45 (C2′)	26.52	32.46	23.05	14.20				
	1-Ethylpentylamine	53.00	38.13 (C2) 31.45 (C2′)	28.88 (C3) 10.83 (C3′)	23.30	14.00					
	1,3-Dimethylpentylamine	44.57	48.02 (C2) 25.14 (C2′)	31.67	30.06 (C4) 19.43 (C4′)	11.34					
C_8	Octylamine	42.54	34.47	27.39	30.02	29.83	32.33	23.10	14.22		
	1-Methylheptylamine	47.13	40.84 (C2) 24.54 (C2′)	26.81	29.92	32.33	23.00	14.21			
	2-Ethylhexylamine	45.02	42.98	31.30 (C3) 24.35 (C3′)	29.62 (C4) 11.24 (C4′)	23.57	14.28				
	1,5-Dimethylhexylamine	47.00	40.95 (C2) 24.49 (C2′)	24.49	39.45	28.16	22.71				
	1,1,3,3-Tetramethylbutylamine	50.94	56.91 (C2) 33.47 (C2′)	31.74	31.74						
C_9	Nonylamine	42.61	34.57	27.42	30.13	30.13	29.28	32.38	23.08	14.25	
	1-Isopropylhexylamine	56.64	35.31 (C2) 33.79 (C2′)	26.70 (C3) 19.51 (C3′) 17.08 (C3″)	32.45	23.07	14.28				
C_{10}	Decylamine	42.59	34.53	27.37	30.08	30.08	30.08	29.82	32.35	23.05	14.23

[a] Taken from: T. D. Brown, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1966.

Table II. C-13 Chemical Shifts (ppm) in Secondary Amines Relative to TMS

	Amine	α	β	γ	δ	ε	ζ	η	θ	ι	κ
C_4	Diethylamine	44.43	15.72								
C_5	*N*-Methyl-*sec*-butylamine	56.64	29.63 (C2) 19.55 (C2′)	10.29							
		33.92 (Me)									
	N-Methyl-*tert*-butylamine	50.40	28.17								
		28.52 (Me)									
C_6	Dipropylamine	52.34	23.94	11.98							
	Diisopropylamine	45.30	23.72								
	N-Ethylbutylamine	49.98	33.14	20.97	14.23						
		44.58	15.73 (Et)								
	N-Ethyl-*sec*-butylamine	54.68	30.17 (C2) 20.31 (C2′)	10.18							
		41.71	16.01 (Et)								
C_7	*N*-Methylhexylamine	52.36	30.54	27.56	32.41	23.15	14.23				
		36.67 (Me)									
	N-Ethylpentylamine	50.04	30.34	29.96	23.00	14.24					
		44.35	15.57 (Et)								
	N-Isopropylbutylamine	47.42	33.34	20.87	14.17						
		48.94	23.41 (*i*-Pr)								
	N-Isopropyl-*sec*-butylamine	51.23	30.39 (C2) 20.56 (C2′)	10.33							
		45.33	23.98 23.28 } (*i*-Pr)								

Table II (*Continued*)

	Amine	α	β	γ	δ	ε	ζ	η	θ	ι	κ
C_8	Dibutylamine	50.11	33.09	20.89	14.20						
	Di-*sec*-butylamine[a]	51.36	30.99, 30.26 (C2)	10.41, 10.11 (C3)							
			21.10, 20.67 (C2′)								
	Diisobutylamine	58.59	28.97	20.78							
	N-Ethylhexylamine	50.12	30.68	27.49	32.25	23.05	14.22				
		44.39	15.60 (Et)								
C_9	*N*-Propylhexylamine	50.29	30.73	27.48	32.26	23.06	14.25				
		52.23	23.76	12.00							
	N-*sec*-Butylpentylamine	47.55	30.90	30.09	23.06	14.26					
		54.75	30.09	10.24 (*sec*-Bu)							
			20.34								
	N-*sec*-Butyl-3-methylbutylamine	45.52	40.30	26.24	22.84						
		54.77	30.07	10.15 (*sec*-Bu)							
			20.33								
	N-*tert*-Butyl-3-methylbutylamine	40.36	40.80	26.05	22.81						
		49.80	29.28 (*t*-Bu)								
	N-Methyl-1,1,3,3-tetramethylbutylamine	53.88	52.66 (C2)	31.80	31.80						
			28.67 (C2′)								
		28.80 (Me)									
C_{10}	Dipentylamine	50.44	30.58	30.09	23.10	14.27					
	N-Butylhexylamine	50.37	30.73	27.48	32.25	23.05	14.25				
		50.02	32.90	20.83	14.23 (Bu)						
	N-*tert*-Butylhexylamine	42.55	31.58	27.50	32.24	22.99	14.20				
		49.94	29.20 (*t*-Bu)								
	N-*sec*-Butyl-3,3-dimethylbutylamine	43.59	45.13	29.83	29.83						
		54.79	30.04	10.15 (*sec*-Bu)							
			20.30								
	Di(3-methylbutyl)amine	48.46	39.93	26.27	22.87						
C_{11}	*N*-Pentylhexylamine	50.37	30.74	27.50	32.27	23.05	14.25				
		50.37	30.45	30.00	23.05	14.25 (Pent)					
	N-Butyl-1-methylhexylamine	53.39	38.18 (C2)	25.98	32.62	23.05	14.20				
			20.84 (C2′)								
		47.16	33.41	20.84	14.20 (Bu)						
	N-Pentyl-1,3-dimethylbutylamine	51.14	47.30 (C2)	25.10	23.17						
			21.21 (C2′)								
		47.70	30.86	30.00	23.17	14.18 (Pent)					
	N-Pentyl-1,2,2-trimethylpropylamine	62.32	34.74 (C2)	26.57							
			15.12 (C2′)								
		49.15	30.89	29.99	22.98	14.27 (Pent)					
	N-(3,3-Dimethylbutyl)pentylamine	50.43	30.45	29.82	22.94	14.19					
		46.44	44.71	29.82	29.82 (3,3-Me_2Bu)						
	N-Butyl-1-ethylpentylamine	58.95	33.99 (C2)	26.93 (C3)	23.45	14.24					
			28.39 (C2′)	9.85 (C3′)							
		46.96	33.48	20.88	14.24 (Bu)						
	Dihexylamine	50.42	30.34	27.53	32.33	23.08	14.21				
C_{12}	*N*-(1,3-Dimethylbutyl)hexylamine	47.66	31.13	27.45	32.21	23.05	14.17				
		51.10	47.33 (C2)	25.08	23.05 (1,3-Me_2Bu)						
			21.19 (C2′)								
C_{13}	*N*-Pentyl-1,1,3,3-tetramethylbutylamine	53.82	53.47 (C2)	31.86	31.86						
			29.52 (C2′)								
		41.94	31.28	29.96	22.90	14.18 (Pent)					
C_{14}	*N*-(1-Ethylpentyl)-1-propylbutylamine	54.02	37.74 (C2)	19.20 (C3)	14.67 (C4)						
			37.58 (C2′)	19.07 (C3′)	14.67 (C4′)						
		55.58	34.40 (C2)	27.34 (C3)	23.47	14.33 (1-EtPent)					
			28.26 (C2′)	9.84 (C3′)							
C_{16}	Dioctylamine	50.40	30.06	27.84	29.92	29.80	32.30	23.03	14.23		
	Di(2-ethylhexyl)amine	53.72	40.21	31.88 (C3)	29.51 (C4)	23.50	14.26				
				25.02 (C3′)	11.22 (C4′)						

[a] Mixture of two diasteriomers. The resonance lines due to each component in the mixture could not be identified because the components were present in nearly equal amount.

Table III. C-13 Chemical Shifts (ppm) in Tertiary Amines Relative to TMS

	Amine	α	β	γ	δ	ϵ	ζ	η	θ	ι	κ	λ	μ
C_3	Trimethylamine	47.56											
C_5	*N*-Methyldiethylamine	51.42	12.83										
		40.97 (Me)											
C_6	Triethylamine	46.92	12.60										
	N,N-Dimethyl-*sec*-butylamine	60.92	26.94 (C2)	11.36									
			13.15 (C2′)										
		40.60 (Me)											
	N,N-Dimethyl-*tert*-butylamine	53.15	25.62										
		38.74 (Me)											
C_8	*N,N*-Dimethylhexylamine	60.11	28.34	27.54	32.34	23.16	14.33						
		45.64 (Me)											
	N,N-Diethylbutylamine	53.21	30.37	20.94	14.22								
		47.43	12.57 (Et)										
	N,N-Diethyl-*sec*-butylamine	56.54	27.52 (C2)	11.78									
			13.93 (C2′)										
		43.44	15.12 (Et)										
	N-Ethyldiisopropylamine	48.27	21.06										
		38.67	17.28 (Et)										
C_9	Tripropylamine	56.76	21.24	12.01									
C_{10}	*N*-Ethyldibutylamine	53.76	30.34	20.92	14.23								
		47.89	12.49 (Et)										
	N,N-Diisopropylbutylamine	44.53	33.75	20.71	14.30								
		48.09	21.00 (*i*-Pr)										
C_{11}	*N*-Methyl-*N*-butylhexylamine	58.19	27.99	27.43	32.25	23.04	14.18						
		57.85	30.20	20.78	14.18 (Bu)								
		42.07 (Me)											
	N-Propyldibutylamine	54.35	30.32	20.90	14.25								
		56.67	21.17	12.04 (Pr)									
	N-Isopropyldibutylamine	49.81	32.01	20.83	14.34								
		50.09	18.15 (*i*-Pr)										
C_{12}	Tributylamine	54.28	30.28	20.96	14.24								
	N-Ethyldipentylamine	54.01	27.75	30.09	23.03	14.26							
		47.86	12.46 (Et)										
	N-Butyldi-*sec*-butylamine[a]	55.04, 54.25 (Cl)	29.65, 28.44 (C2)	12.17 (*sec*-Bu)									
			18.28, 17.19 (C2′)										
		44.73, 44.29 (C1)	33.30, 32.90 (C2)	20.87	14.34 (Bu)								
	N-*tert*-Butyldibutylamine	50.68	34.60	20.77	14.32								
		54.49	27.43 (*t*-Bu)										
C_{13}	*N,N*-Dibutyl-3-methylbutylamine	52.54	36.98	26.31	22.92								
		54.18	30.21	20.84	14.22 (Bu)								
C_{14}	*N,N*-Dibutylhexylamine	54.54	27.96	27.48	32.26	23.05	14.20						
		54.24	30.24	20.63	14.20 (Bu)								

	N,N-Dibutyl-3,3-dimethylbutylamine	50.22	41.08	29.69	30.04								
		54.27	30.28	20.94	14.28 (Bu)								
	N-sec-Butyldipentylamine	50.07	29.51	30.04	23.09	14.31							
		56.84	27.40	11.96 } (*sec*-Bu)									
			13.70										
	N,N-Dibutyl-1-methylpentylamine	54.85	34.31 (C2)	29.72	23.25	14.35							
			14.10 (C2′)										
		49.81	32.10	20.89	14.35 (Bu)								
C_{15}	Tripentylamine	54.50	27.63	30.05	22.98	14.24							
	Tri(3-methylbutyl)amine	52.38	36.84	26.29	22.92								
	N,N-Dibutylheptylamine	54.56	28.01	27.79	29.72	32.34	23.01	14.23					
		54.26	30.24	20.87	14.23 (Bu)								
	N-Butyl-*N*-(1,2,2-trimethylpropyl)pentylamine	52.79	29.30	29.99	23.10	14.28 (Pent)							
		52.56	31.88	20.95	14.28 (Bu)								
		64.41	35.74	27.74									
			7.74										
	N,N-Di-*sec*-butylheptylamine[a]	45.29 } (C1)	31.05 } (C2)	28.20	30.24	32.83	23.44	14.62 } (Hept)					
		45.69 }	31.45 }										
		55.44 } (C1)	28.82 } (C2)	12.55 } (*sec*-Bu)									
		54.65 }	30.02 }										
			18.67 } (C2′)										
			17.59 }										
C_{16}	*N,N*-Dipentyl(1,3-dimethylbutyl)amine	52.40	44.14 (C2)	24.92	22.81 (C4)								
			14.03 (C2′)		23.30 (C4′)								
		49.96	29.49	30.01	23.03	14.28 (Pent)							
	N,N-Dibutyl(1,1,3,3-tetramethylbutyl)amine	58.50	49.96 (C2)	31.39	32.13								
			27.93 (C2′)										
		50.48	34.50	20.86	14.32 (Bu)								
	N-Butyl-*N*-hexyl(1,3-dimethylbutyl)amine	52.42	44.12 (C2)	24.98	22.85 (C4) } (1,3-Me_2Bu)								
			14.05 (C2′)		23.32 (C4′) }								
		50.03	29.84	27.52	32.31	23.12	14.30						
		49.76	32.11	20.89	14.30 (Bu)								
C_{17}	*N*-Butyl-*N*-pentyl(1,1,3,3-tetramethylbutyl)amine	58.71	50.13 (C2)	31.54	32.27								
			28.10 (C2′)										
		50.99	32.27	30.23	23.15	14.45 (Pent)							
		50.71	34.73	21.07	14.45 (Bu)								
C_{18}	Trihexylamine	54.54	27.96	27.51	32.27	23.07	14.22						
C_{20}	*N*-Butyldi-2-ethylhexylamine	60.19	37.93	31.65 (C3)	29.48 (C4)	23.55	14.25						
				24.77 (C3′)	10.98 (C4′)								
		55.14	29.83	21.00	14.25 (Bu)								
C_{24}	Trioctylamine	54.50	27.87	27.87	30.00	29.75	32.25	22.98	14.28				
C_{36}	Tridodecylamine	54.48	27.96	27.79	30.05	30.05	30.05	30.05	30.05	29.72	32.36	22.94	14.18

[a] Mixture of two diastereomers. The resonance lines due to each component in the mixture could not be identified because the components were present in nearly equal amount.

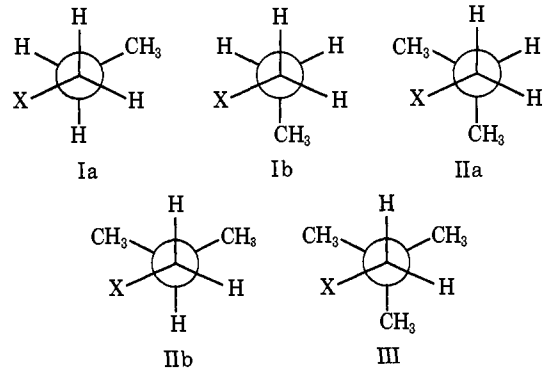


Figure 1. Conformations of propyl-X (I), isobutyl-X (II), and 2,2-dimethylpropyl-X (III).

Table IV. Linear Correlations between the Carbon Chemical Shifts of Amines and the Corresponding Hydrocarbon[a]

$$\delta_c^{\text{amine}} = (\delta_c^{\text{alkane}} A) + B$$

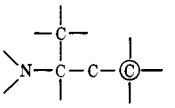
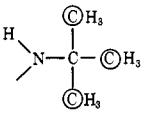
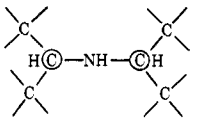
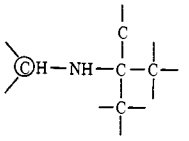
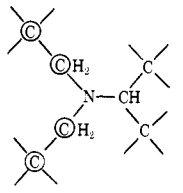
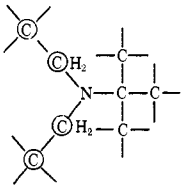
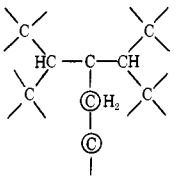
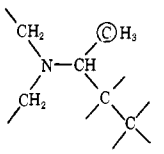
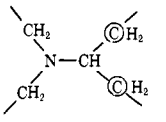
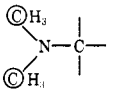
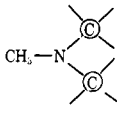
	1[c]			2[c]		
	A	*B*	sd[b]	*A*	*B*	sd[b]
Primary Amines						
α carbon atoms	0.846	23.09	0.30	0.846	23.09	0.30
β carbon atoms	0.955	3.00	0.56	0.955	3.14	0.32
γ carbon atoms	0.941	−0.07	0.32	0.951	−1.08	0.26
Secondary Amines						
α carbon atoms	0.900	22.88	0.88	0.850	24.70	0.42
β carbon atoms	0.942	2.07	0.67	0.958	1.77	0.39
γ carbon atoms	0.951	−0.68	0.66	0.950	−0.94	0.34
Tertiary Amines						
α carbon atoms	0.914	22.62	1.33	0.938	21.91	0.55
β carbon atoms	0.999	0.45	1.61	0.946	1.79	0.63
γ carbon atoms	0.934	−0.43	0.86	0.966	−1.60	0.33

[a] The corresponding hydrocarbon is that in which the amino nitrogen is replaced by a CH. [b] Standard deviation in ppm for prediction of amine chemical shifts. [c] Set 1 applies to the uncorrected alkane chemical shifts; set 2 applies to the corrected alkane chemical shifts (see text).

group.[8,11,13-15] Roberts, *et al.*,[8] have suggested that in alcohols this difference is caused by a somewhat greater steric effect of a hydroxyl group compared with a methyl group, although they point out that studies[16] of conformational equilibria in cyclohexane derivatives show the opposite. If the effect of a polar group were greater than that of a CH_3 one would expect this difference to increase with increasing number of γ carbon atoms, since these should cause more gauche interactions per γ carbon atom. A constant difference of 1.8 ppm is, however, observed for propylamine, isobutylamine, and 2,2-dimethylpropylamine relative to the corresponding alkanes. Similar results are found by examination of the chemical shifts given for alcohols.[8] This then indicates that at least a part of the difference may be caused simply by a change in conformational equilibrium giving more gauche interactions relative to the alkane. Unfortunately, only a few data have been reported for conformational equilibria around the C^{α}–C^{β} bond in amines or alcohols. In Figure 1 the most stable conformations of propyl-X (I), isobutyl-X (II), and 2,2-dimethylpropyl-X (III) are shown. From the latter

(13) R. Hagen and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 4504 (1969).
(14) T. Pehk and E. Lippmaa, *Org. Magn. Resonance*, **3**, 679 (1971).
(15) G. Engelhardt, E. Lippmaa, and T. Pehk, *J. Prakt. Chem.*, **312**, 935 (1970).
(16) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

Table V. Correctional Terms (See Text)

Substructure[a]	Corr,[a] ppm
	primary amines: +1.80 secondary amines: +0.90 tertiary amines: +2.00
	primary amines: −1.75 secondary amines: −1.75
	−1.65
	−3.80
	−2.00 ppm to α carbon atoms (also if one or both are methyl groups) +1.70 ppm to β carbon atoms
	+1.60 ppm to α carbon atoms +4.10 ppm to β carbon atoms
	−4.50 ppm to α carbon atoms +2.95 ppm to β carbon atoms
	−4.50
	−2.15
	+2.45
	+1.55 ppm (does not apply to methyl groups)

[a] The values given represent the correction to the value calculated for the circled carbon in the corresponding alkane. Open ended bonds may connect to carbon or hydrogen atoms.

Table VI. Changes of C-13 Chemical Shifts (ppm) upon Replacement of an Amino Group by a Hydrogen Atom

$$R\text{-}NH_2 \longrightarrow R\text{-}H^a$$

Amine	α	β	γ	δ
Methylamine[c]	30.4			
Ethylamine[c]	30.9	13.0		
Propylamine[b]	29.0	11.3	−4.2	
Butylamine[b]	29.1	11.8	−4.5	0.1
Pentylamine	28.8	11.7	−4.8	0.5
Hexylamine	28.6	11.5	−4.9	0.3
Heptylamine	28.5	11.5	−5.0	0.4
Octylamine	28.6	11.4	−5.1	0.3
Nonylamine	28.4	11.5	−4.9	0.4
Decylamine[b]	28.5	11.3	−5.0	0.2
3-Methylbutylamine	28.7	11.8	−4.4	0.6
Isopropylamine[b]	26.9	10.9		
sec-Butylamine[b]	24.0	8.3 (C2)	−2.4	
		10.3 (C2′)		
1-Methylbutylamine	24.3	8.3 (C2)	−2.7	0.5
		10.2 (C2′)		
1-Methylhexylamine	24.2	8.5 (C2)	−2.8	0.1
		10.4 (C2′)		
1-Methylheptylamine	24.1	8.4 (C2)	−2.9	0.2
		10.6 (C2′)		
1,3-Dimethylbutylamine	23.6	9.9 (C2)	−3.1	0.3
		10.5 (C2′)		
1,3-Dimethylpentylamine	24.0	8.7 (C2)	−3.0	0.2 (C4)
		10.9 (C2′)		0.3 (C4′)
1,5-Dimethylhexylamine	23.9	8.2 (C2)	−3.1	−0.2
		10.3 (C2′)		
tert-Butylamine[b]	22.0	8.7		
Isobutylamine[b]	26.4	7.9	−5.0	
2-Methylbutylamine	27.1	8.3	−4.8 (C3)	−0.3
			−5.1 (C3′)	
2-Ethylhexylamine	25.4	7.9	−5.6 (C3)	−0.4
			−5.7 (C3′)	−0.4
2,2-Dimethylpropylamine	22.5	3.7	−5.0	
2,2-Dimethylbutylamine	23.4	4.0	−5.0 (C3)	−0.1
			−4.7 (C3′)	
1,2,2-Trimethylpropylamine	18.8	3.7 (C2)	−3.1	
		9.9 (C2′)		
1,1,3,3-Tetramethylbutylamine	25.3	3.3 (C2)	0.5	1.5
		8.4 (C2′)		
1-Ethylpentylamine	20.7	8.8 (C2)	−3.5 (C3)	0.4
		8.5 (C2′)	−3.2 (C3′)	
1-Isopropylhexylamine	17.1	7.5 (C2)	−3.4 (C3)	0.1
		5.4 (C2′)	−3.1 (C3′)	

[a] Alkane experimental data taken from ref 6 and corrected for solvent (see text). [b] Alkane experimental data taken from D. M. Grant and E. G. Poul, *J. Amer. Chem. Soc.*, 86, 2984 (1964). [c] Alkane experimental data taken from H. Spiesecke and W. G. Sneider, *J. Chem. Phys.*, 35, 722 (1961).

compound (III) it is possible to estimate the magnitude of a gauche CH_3/X nonbonded interaction, as the three stable conformations of this molecule are identical. Using this value and the substituent parameters given in Table VI, it is possible, by the same method as has been used for cyclohexane derivatives,[17] to obtain an estimate of the equilibrium distribution of rotamers in propylamine (Ia *vs.* Ib) and isobutylamine (IIa *vs.* IIb). The result is that both compounds show a statistical distribution of these two possible conformations. Scott[18] reported the same result for propylamine, obtained by statistical thermodynamic treatment of its molecular spectrum. Statistical distribution is also estimated for 1-propanol and 2-methyl-1-propanol using reported[8] chemical shift data. This is quite different from the rotamer distribution found for the corresponding alkanes, where it has been shown that butane has two molecules in the trans rotamer for each in the gauche,[19] and that isopentane has 10% of its molecules in the all gauche conformation.[20] Using the values found above for the gauche CH_3/NH_2 and CH_3/OH nonbonded interactions one can then estimate the shift to be expected in propylamine and 1-propanol if both molecules have the same conformational distribution as does butane. The values of 2.5 and 2.4 ppm, respectively, compared with the γ shift in butane of 2.4 ppm, show that there should be no big difference in the steric effects of a CH_3 group, compared to an NH_2 or OH group. On the other hand, calculation in this manner of CH_3/CH_3 gauche interactions gives results that vary according to the choice of model compound; *e.g.*, the cmr spectrum of 2,2-dimethylbutane yields a value of 4.4 ppm for the gauche interaction, while calculations based on butane (using the known conformational distribution)[19] results in a value of 6.9 ppm. Similar discrepancies are also found for various methyl-substitued cyclohexanes.[9,10] This inconsistency for hydrocarbons may be caused by the repulsive nature of the C–C nonbonded 1–4 interaction, leading to decreased stability of gauche conformers. These interactions may be sufficiently large to cause the geometry of the gauche rotamer to change slightly, and thereby change the carbon chemical shifts from that of the idealized tetrahedral carbon with a dihedral angle of 60°.

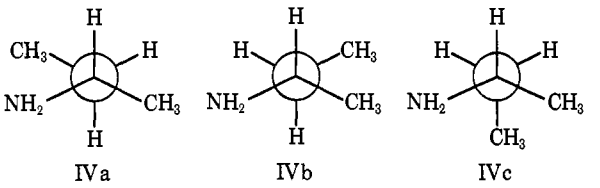


Figure 2. Conformations of *sec*-butylamine.

For both primary, secondary, and tertiary amines a decrease in the γ shift is found when the *N*-alkyl groups are secondary or tertiary rather than primary, as is expressed in the corrective term introduced above for these compounds (Table V). This appears to be a rather general feature as it is also found when examining the data given for OH,[8] Cl,[15] Br,[15] or NH_3^+.[21] These findings may be rationalized for amines by assuming the CH_3/NH_2 and CH_3/CH_3 1–4 nonbonded steric interactions to be about the same. The different conformations possible for *sec*-butylamine (IV) are shown in Figure 2. The γ methyl group in this compound is found to be only 0.7 ppm more shielded than the corresponding methyl group in isopentane. Furthermore, the change in chemical shift of the β methyl group in going from isopropyl- to *sec*-butylamine is very much the same as that observed in going from isobutane to isopentane (2.5 and 2.3 ppm, respectively), indicating that the amount of $CH_3^{\beta}/CH_3^{\gamma}$ gauche interaction is about the same in *sec*-butylamine and the corresponding alkane. This means that the con-

(17) G. W. Buchanan, J. B. Stothers, and Siu-TzyyWu, *Can. J. Chem.*, 47, 3113 (1969); G. W. Buchanan and J. B. Stothers, *Can. J. Chem.*, 47, 3605 (1969).
(18) D. W. Scott, *J. Chem. Thermodyn.*, 3, 843 (1971).
(19) G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, 18, 51 (1950).
(20) D. J. Millen, *Progr. Stereochem.*, 3, 157 (1962).
(21) H. Eggert and C. Djerassi, to be submitted for publication.

formational equilibrium must be about the same in *sec*-butylamine and in isopentane, and hence explains the small difference observed in the shieldings of their γ carbon atoms.

In summary, the results presented show that C-13 nmr may be useful in studying rotational isomerism and make it possible to predict C-13 nmr spectra of unknown amines. In conjunction with mass spectral data it should be possible to perform unambiguous structure assignment on such unknowns, which will be an impressive achievement when it is recalled that, *e.g.*, the molecular formula $C_{21}H_{45}N$ corresponds[5] to over 38 million structural isomers.

Acknowledgment. The nmr spectrometer was purchased under Grant No. GP-28142 from The National Science Foundation. Financial assistance by Grant No. RR-612-01 from the National Institutes of Health is also gratefully acknowledged.

Carbon-13 Magnetic Resonance. XXIII.[1] The Methyldecalins

Don K. Dalling, David M. Grant,* and Edward G. Paul

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received August 21, 1972*

Abstract: The proton-decoupled carbon-13 magnetic resonance (cmr) spectra have been obtained for *cis*- and *trans*-decalin, six of the possible ten monomethyldecaline, five available dimethyldecalins, and spiro[5.5]undecane. The resonance lines are assigned using previously developed methyl substituent parameter sets, with the aid of intensity arguments, and selective decoupling. A multiple regression analysis is executed on the data to develop a new and simpler set of substituent and conformational parameters applicable to aliphatic hydrocarbons in general.

Decahydronaphthalene (decalin) became a molecule of stereochemical interest shortly after the postulation of tetrahedral carbon,[2,3] Although it was thought for some time that only the cis isomer was possible, Sachse[4] predicted that cis and trans ring junctures were reasonable, and that several strain-free conformational isomerides would result from stable chair–boat combinations. Mohr created a controversy by proposing that, at ordinary temperatures, thermal energy was sufficient to interconvert chair and boat forms of cyclohexane, so that only two isomers of decalin would be isolable, as a result of the two kinds of ring junction.[5] He suggested that the chair–chair form of *trans*-decalin had the lowest energy, and that the boat–boat isomer of *cis*-decalin was most favorable. The Sachse–Mohr concept that *cis*-decalin exists primarily in a two-boat form was held for many years, until Bastiansen and Hassel used electron diffraction techniques to demonstrate that *cis*-decalin exists predominantly in a two-chair form.[6,7]

A comparison of models of the two decalin isomers reveals that *cis*-decalin has three steric interactions of the type found in the gauche conformation of *n*-butane which are not present in the trans compound. In previous papers in this series,[8,9] the evidence relative to the energetics of gauche interactions was discussed. It was concluded that the energy gained by a molecule for each gauche interaction is about 0.7–1.2 kcal/mol. Experimental measurements of the standard heats of combustion of *cis*- and *trans*-decalin have resulted in determination[10–12] of the standard heats of formation (in kcal/mol) as follows.

	Liquid	Gas
cis	-52.45 ± 0.22	-40.45 ± 0.22
trans	-55.14 ± 0.22	-43.54 ± 0.55
difference	2.69 ± 0.31	3.09 ± 0.59

These results are seen to be in agreement with the 0.7–1.2 kcal/mol of energy gained for each of the three gauche interactions. It is noted that the trans isomer is conformationally locked, while in the cis compound interconversion between equivalent chair–chair structures is possible.

The 9-methyldecalins are of biochemical interest, because they are commonly encountered as fragments of natural products. Measurement of thermodynamic properties[13] indicated standard free energies of formation of -58.31 ± 0.47 kcal/mol for *cis*-9-methyldecalin and -59.70 ± 0.44 kcal/mol for the *trans*-9-methyl isomer. The difference of 1.39 ± 0.64 kcal/mol is in agreement, within the limits of its uncertainty, with the postulated energy increment due to the one gauche interaction difference between the two compounds.

Methyl substitution on *cis*-decalin at positions other

(1) Previous paper in series: R. J. Pugmire, D. M. Grant, L. B. Townsend, and R. K. Robins, *J. Amer. Chem. Soc.*, **95**, 2791 (1973).
(2) J. H. van't Hoff, *Arch. Neer. Sci. Exactes Natur.*, **9**, 445 (1874).
(3) J. A. Lebel, *Bull. Soc. Chim. Fr.*, **22**, 337 (1874).
(4) H. Sachse, *Ber.*, **23**, 1363 (1890); *Z. Phys. Chem. (Liepzig)*, **10**, 203 (1892).
(5) E. Mohr, *J. Prakt. Chem.*, [2], **98**, 315 (1918); *Ber.*, **55B**, 230 (1922).
(6) O. Hassel, *Tidsskr. Kjemi, Bergv. Met.*, **3**, 32 (1943).
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(8) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967), and references therein.
(9) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **94**, 5318 (1972).
(10) G. F. Davies and E. C. Gilbert, *J. Amer. Chem. Soc.*, **63**, 1585 (1941).
(11) D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, **64**, 1723 (1960).
(12) T. Miyazawa and K. S. Pitzer, *J. Amer. Chem. Soc.*, **80**, 60 (1958).
(13) W. G. Dauben, O. Rohr, A. Labbauf, and F. D. Rossini, *J. Phys. Chem.*, **64**, 283 (1960).