Hydrogen Bonding and Related Association in Linear Aliphatic Amino Alcohols as Probed by Carbon-13 Spin–Lattice Relaxation Times

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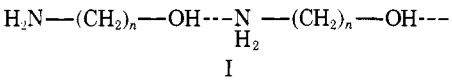
Abstract: Carbon-13 chemical shifts and spin-lattice relaxation data obtained in a number of solvents for five linear aliphatic amino alcohols are presented. The purpose of monitoring the relaxation behavior was to learn about inter- and intramolecular association as a function of concentration and solvent. An analyses of the T_1 data reveals that intermolecular OH-OH hydrogen bonding competes efficiently with OH-NH hydrogen bonding in neat solution and in chloroform solution. Moreover, overall diffusion is slower in 2-aminoethanol than for the next few homologues in these media. This observation is in agreement with certain ir studies where intermolecular hydrogen bonding has been shown to be more favorable in cases like 2-aminoethanol. The results presented for water and dimethyl sulfoxide solutions reveal that intermolecular solute-solute interactions decrease; for 6-aminohexanol the T_1 pattern gives evidence for tumbling via an open-chain structure. Finally, the agreement between calculated T_1's, using a basic isotropic diffusion model and experimental data, is briefly discussed.

Hydrogen bonding of molecules having two nucleophilic sites, like amino alcohols, is of a potential interest since multiplicity of proton donor and acceptor positions is prevalent in many biological systems. The competition between inter- and intramolecular hydrogen bonding has received special attention, being the subject of several infrared studies.[2] Based on the magnitude of the OH frequency shifts, DeRoos and Bakker[3] demonstrated that the binding energy of the intramolecular hydrogen bond increased going from a five-membered ring to a six- or seven-membered ring. Also, a concentration dependence was noticeable only when studying solutions of 2-aminoethanol or its mono-*N*-alkyl-substituted derivatives, indicating significant intermolecular association in these cases.

Besides the fact that all of these investigations were restricted to certain inert solvents, the ir results gave only limited information about the solution structure. Strong hydrogen-bonding results in broad absorption peaks, which causes important bands to overlap and consequently the interpretation is very complicated. For example, the existence of intramolecular hydrogen bonds in solutions of 2-aminoethanol,[2a,c,3] as well as the competition between OH-NH and NH-OH hydrogen bonds, are subjects that have caused a great deal of controversy, which can in part be ascribed to such experimental difficulties.

In the case of aliphatic primary or secondary amino alcohols several types of inter- and intramolecular associations may exist. However, it is safe to assume[2j] that the amino group plays a minor role as a hydrogen-bond donor, which leaves the following possibilities:



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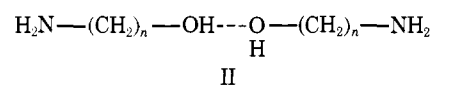

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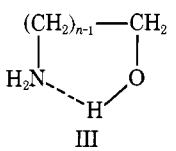

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The strength of the intramolecular hydrogen bond depends of course on the nature of the bonding atoms and the resulting ring size.

It is a well-known fact that measurements of ^{13}C spin–lattice relaxation times (T_1's) can provide valuable information about association phenomena and motional behavior in liquids.[4] The extent to which intermolecular or interionic interactions hamper the mobility of molecules was initially demonstrated by Allerhand et al. studying 1-decanol,[5] and later similar reports[6] have extended this work to cover a variety of monofunctional aliphatic compounds. The existence of intermolecular association causes a restriction in overall tumbling motion of the molecule allowing observation of chain segmental motion as one moves away along the chain from the polar "fixed" site. Largely because the T_1 measurements are time consuming only a few investigations in this area have been undertaken to examine ^{13}C T_1 behavior as a function of concentration and solvent.[6f,g,h]

The aim of the present study is to probe the dynamics of several aliphatic linear amino alcohols by means of T_1 measurements in order to get some insight about important aggregation and medium effects. Obviously these studies will not cover the same solute concentration range as used for the earlier ir investigations but variation of concentration will still be an important complement to these studies.

Experimental Section

The amino alcohols were obtained from commercial sources (Aldrich Chemical Co. and Columbia Organic Chemicals Co.). 6-Aminohexanol was recrystallized from carbon tetrachloride and the liquid amino alcohols were purified by distillation after standing over anhydrous calcium sulfate. Unfortunately, the amino alcohols studied have very limited solubility in conventional inert solvents and chloroform, being the least dissociating solvent used, is by no means ideal for hydrogen-bonding studies, since it may form hydrogen bonds to the solute. All viscosities were measured using Cannon-Manning semimicro viscosimeters.

Both ^{13}C chemical shifts and spin-lattice relaxation times were obtained at 67.9 MHz and at 36 ± 2 °C with complete proton decoupling. Samples were contained in 10 mm o.d. tubes or in 8 mm o.d. tubes with a deuterium lock solvent used as an annulus in a concentric 10-mm tube. The T_1's were calculated from PRFT spectra using the inversion recovery pulse sequence $(T\text{-}180°\text{-}\tau\text{-}90°_\infty)_n$. A representative result, shown as a "stacked" plot, is given in Figure 1. Three totally relaxed spectra (τ_∞ spectra) were obtained for accurate calculation of T_1's. The width of a 90° ^{13}C pulse was ~17 μs and a 5000 Hz spectral width was used in all cases (8K transforms).

The reproducibility was determined to be better than ±10% in all runs; for solutions ≥2 M reproducibility was *considerably* better. At least two runs were performed for each sample. Duplicate sets of data are given in Table II for representative experiments. At high con-

Table I. ^{13}C Chemical Shifts of Linear Amino Alcohols[a]

	C_1	C_2	C_3	C_4	C_5	C_6
2-Aminoethanol	63.3 (−7.0)[b]	44.0 (−4.8)				
3-Aminopropanol	60.6 (+0.9)	35.3 (−2.1)	39.8 (+0.5)			
4-Aminobutanol	61.7 (−0.1)	30.7 (−0.1)	30.2 (−1.0)	41.7 (−1.3)		
5-Aminopentanol	61.6 (−0.5)	32.7 (−0.6)	23.2 (−0.5)	33.3 (−1.3)	42.0 (−0.9)	
6-Aminohexanol	61.7 (−0.5)	32.8 (−0.3)	25.8 (−0.6)	26.8 (−0.6)	33.4 (−1.2)	41.9 (−1.2)

[a] 2 M in chloroform-*d*. Temperature 36 ± 1 °C. In parts per million relative to internal TMS. [b] Values in parentheses are $\Delta\delta = \delta_c^{obsd} - \delta_c^{calcd}$ (see text), assuming additivity of substituent.

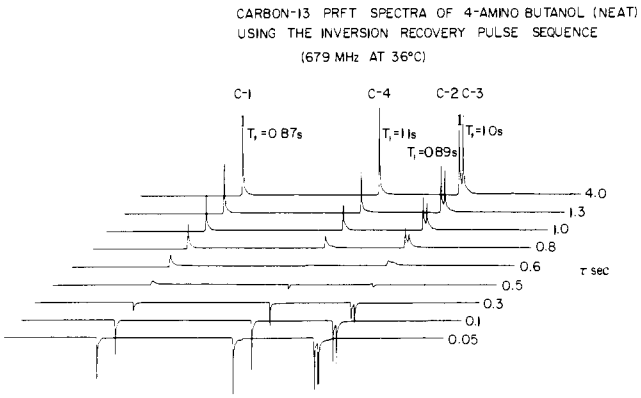

Figure 1. T_1 measurement of 4-aminobutanol presented as a stacked plot. Number to the right of each spectrum is the delay time, τ (40 scans, 4285 Hz shown).

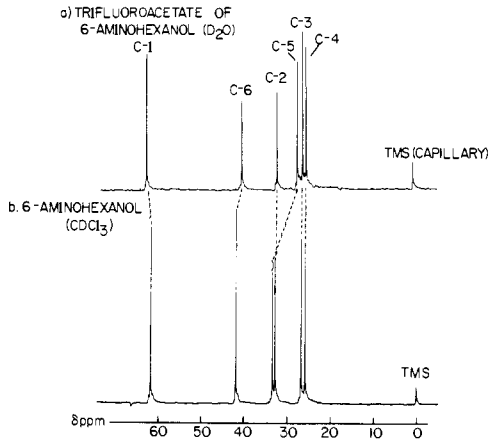

Figure 2. Proton-decoupled carbon-13 FT spectra of 6-aminohexanol and its trifluoroacetate.

centrations the main error between runs is probably due to the difficulties in exactly reproducing the sample temperature. Temperature deviations at 36 °C of ±2 °C can produce systematic variation in T_1's of ~10% for associated molecular systems.[7] Keeping the cooling conditions and the applied decoupling power constant, a small but significant temperature change is produced by varying the solvent. For concentrated solutions we tried to overcome this problem by performing consecutive runs keeping the same solvent and varying the substrate. Thus the given T_1's at neat or 2 M concentrations were run at identical settings in each solvent. Sample temperatures were measured before and immediately after each T_1 run, using a thermometer preheated to the approximate temperature of the sample. The temperature measurements were made after rapidly removing the sample from the probe, approximate temperature being obtained from a thermocouple located in the probe just below the sample. No significant temperature gradients were noted with the low levels (<3 W) of decoupling power used.

Results and Discussion

A. Carbon-13 Chemical Shifts. The carbon-13 chemical shifts for all studied amino alcohols are listed in Table I along with values representing deviations from calculated chemical shifts. The calculated differentials were obtained by applying earlier reported amino substituent parameters[8] to chemical shifts of aliphatic alcohols.[9] As seen from the results in Table I our experimentally determined shifts are in close correspondence with the calculated values except for carbons α and β to the amino groups. This result is expected for hydrogen-bonded systems since it is well known that nearby carbons and especially β carbons are very sensitive to changes in the electronic environment of the nitrogen atom.[10] Significant changes in shielding have been reported for β carbons in saturated systems upon protonation of the amino group.[10] This fact has been utilized to make the assignment of the inner carbons of the studied amino alcohols. Addition of trifluoroacetic acid to a chloroform solution of the higher homologues listed in Table I causes a marked upfield shift for the β-N carbon allowing separation from the unaffected C-2 peak. Thus we were able to distinguish between the C-2 and C-3 carbons in 4-aminobutanol, the C-2 and C-4 carbons in 5-aminopentanol, and also the peaks from C-2 and C-5 in 6-aminohexanol. Figure 2 gives an illustration of the shielding changes caused by protonation of the amino group in 6-aminohexanol. These perturbations of the shielding must be kept in mind if changing the solvent system. In the solutions of the 5-amino and 6-amino derivatives we observed that the relative positions of the β-N carbon and the C-2 carbon were interchanged going from a chloroform to an aqueous solution. The assignment of the C-3 and C-4 carbons in 6-aminohexanol was *solely* based on the relative positions obtained from the calculation.

Additional evidence for the proposed chemical shift assignment was obtained by utilizing the regularly increasing trend in T_1's obtained by proceeding along the chain away from the hydroxyl group (for the compounds dissolved in $CDCl_3$).

B. Carbon-13 Spin–Lattice Relaxation Times. A species that is hydrogen bonded to its neighbors has a longer rotational correlation time and a smaller self-diffusion coefficient than a nonbonded species of similar molecular weight and size. This follows from the well-known Stokes–Einstein expression[11] which modified by Gierer and Wirtz[12] can be written

$$\tau_c = \frac{4\pi\eta(r_I^*)^3}{3kT} f_r = \frac{V_m^* f_r \eta}{kT} \quad (1)$$

where r_I^* is the radius of the species, V_m^* its molecular volume, η is the observed macroscopic viscosity, and f_r is a correction factor defined as:[12]

$$f_r = [6(r/r_I^*) + (1 + r/r_I^*)^{-3}]^{-1} \quad (2)$$

where r is the radius of the surrounding solvent molecules. The factor f_r, often denoted as the microviscosity factor, is introduced to account for the observation that the Stokes–Einstein equation overestimates the magnitude of the rotational friction constant by at least one order of magnitude in certain cases.[13]

Table II. ^{13}C Spin-Lattice Relaxation Times of Linear Amino Alcohols

Solution	η, cP[a]	T_1, s[b] C_1	C_2	C_3	C_4	C_5	C_6
2-Aminoethanol							
Neat	11.9	0.61	0.71				
2 M in $CDCl_3$	0.75	2.1	2.3				
0.5 M in $CDCl_3$	0.54	4.5	4.8				
0.1 M in $CDCl_3$	0.52	5.2[c]	5.3[c]				
2 M in H_2O	1.0	5.0	5.3				
0.5 M in H_2O	0.89	5.3	5.7				
		5.4	5.3				
2 M in DMSO-d_6	1.8	2.3	2.4				
		2.5	2.5				
0.5 M in DMSO-d_6	1.7	5.4	5.2				
3-Aminopropanol							
Neat	16.5	1.1	1.2	1.3			
2 M in $CDCl_3$	0.81	3.5	3.8	4.1			
0.5 M in $CDCl_3$	0.58	7.0	7.4	7.0			
0.1 M in $CDCl_3$	0.52	7.6[c]	6.7[c]	7.7[c]			
2 M in H_2O	1.2	5.0	5.2	5.2			
0.5 M in H_2O	0.90	5.2	5.8	5.5			
2 M in DMSO-d_6	2.0	2.9	2.9	2.9			
		3.1	3.0	2.9			
0.5 M in DMSO-d_6	1.8	5.2	*d*	5.2			
		5.4	*d*	5.5			
4-Aminobutanol							
Neat	19	0.87	0.89	1.0	1.1		
		0.87	0.95	0.90	1.0		
2 M in $CDCl_3$	0.91	3.3	3.7	3.8	3.9		
2 M in H_2O	1.4	4.0	4.3	4.3	4.2		
2 M in DMSO-d_6	2.2	2.1	2.0	2.1	2.2		
		2.2	2.2	2.0	2.3		
5-Aminopentanol							
Neat	21	0.78	0.77	0.82	0.85	0.99	
2 M in $CDCl_3$	1.1	2.5	2.5	2.7	3.0	3.3	
2 M in H_2O	1.6	3.3	3.0	2.9	3.3	3.3	
2 M in DMSO-d_6	2.3	1.8	1.8	1.9	2.0	2.0	
		1.9	1.8	2.0	1.9	2.1	
6-Aminohexanol							
2 M in $CDCl_3$	1.3	1.8	1.8	2.0	2.0	2.2	2.4
2 M in H_2O	1.7	2.5	2.1	1.8	1.7	1.8	2.0
2 M in DMSO-d_6	2.6	1.8	1.6	1.4	1.3	1.5	1.8

[a] Viscosities measured at 36 °C. [b] Estimated accuracies ±10% (see text). [c] Single run; FIRFT sequence (D. Canet, G. C. Levy, and I. R. Peat, *J. Magn. Reson.*, **18**, 199 (1975)); estimated accuracy ±15-20%. [d] T_1 uncertain due to overlapping signals from solvent.

In cases where the residence time τ_H is long compared with the rotational correlation time τ_c, but short relative to T_1, the quantity r_I* is the mean radius of the different aggregates[14-16]

$$(r_I^*)^3 = \sum_{I=0}^{n} P_I r_I^3 \qquad (3)$$

where P_1 is the probability that a given molecule is hydrogen bonded to one neighbor, P_2 that the molecule is bonded to two neighbors, etc. The factors r_I are the radii of the various formed aggregates. Under these conditions of exchange we are observing an averaged correlation time and this time is mainly influenced by the presence of large aggregates. In other words we are unable to probe the individual types of molecular diffusion present; instead we see only a *mean* result of the dynamic process. Besides the explicit dependence on the effective radius in eq 1 the particle size also enters implicitly in a more hidden form in the microviscosity, ηf_r. Problems associated with the fact that macroscopic viscosities and relaxation times are not monitoring solution structure *in the same way* have been subject to considerable attention.[4a] It must be remembered that the macroscopic viscosity is averaged over the entire solution, but the rotational correlation time is sensitive to local fluid conditions that can contribute significantly to τ_c for individual species.[13,6h] This could be responsible for the marked anomalies in solutions of nonuniform particles such as associated liquids.

Before proceeding any further we must remember under what conditions eq 1 was originally derived. Hydrodynamic theories assume that the particles are spherical tops undergoing small-step Brownian motion. Furthermore, the rotational diffusion must be isotropic and occur under stick boundary conditions, which means that the surrounding solvent molecules rotate with the immersed particle. Thus reasonable agreement between T_1^{obsd} and T_1^{calcd} (hydrodynamic) has been found only for large solute molecules, relative to the solvent molecules, and very highly associated liquids like water.[13]

The discrepancy that is found between theory and experiment is normally removed by the mentioned empirical correction factor, f_r. For neat liquids this factor equals $\sim 1/6$ using expression 2. However, earlier investigations[13b] have shown that this value results in a calculated T_1 which serves only as a lower limit for the observed relaxation times. For a large number of associated or nonassociated organic liquids a microviscosity factor of $1/12$ normally fits experimental data better.[13b]

It is thus of interest in our case to estimate the relative

Table III. T_1 Temperature Dependence

Compd	Temp, °C[a]	T_1, s[b] C_1	C_2	C_3	C_4	E_a, kcal mol^{-1}[c]
2-Aminoethanol	13	0.29	0.34			
	28	0.64	0.65			6.8 (C_1)
	58	1.5	2.1			7.4 (C_2)
	78	3.2	3.8			
3-Aminopropanol	23	0.52	0.54	0.54		7.3 (C_1)
	40	0.98	1.14	1.02		7.4 (C_2)
	62	2.2	2.4	2.2		7.3 (C_3)
	85	4.4	4.7	4.4		
4-Aminobutanol	13	0.31	0.30	0.31	0.34	7.6 (C_1)
	28	0.71	0.68	0.31	0.34	7.6 (C_2, C_3)
	58	2.4	2.5	2.5	2.7	7.8 (C_4)
	78	3.8	3.6	3.6	4.2	

[a] Temperatures ±2 °C, see text. [b] T_1's ±5-10%. [c] Calculated from Arrhenius theory, maximum error ±1 kcal mol^{-1}, probable accuracy ±0.6 kcal/mol.

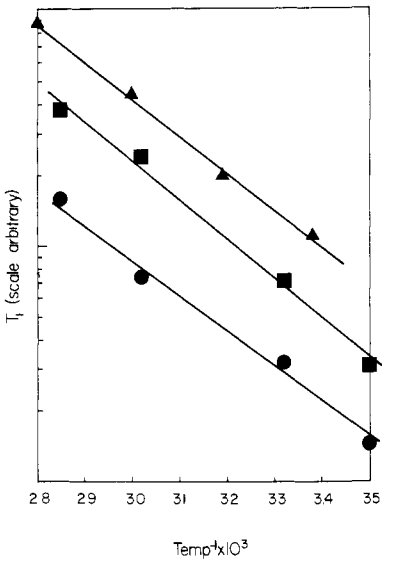

Figure 3. Variation with temperature of ^{13}C T_1's for the 1 carbons of three amino alcohols: (●) 2-aminoethanol; (▲) 3-aminopropanol; (■) 4-aminobutanol.

magnitudes for the T_1's of 2-aminoethanol and 3-aminopropanol, assuming the same degree of internal motion and the same microviscosity factor $\approx 1/6$. We can get an estimation of the molecular volume in eq 1 using eq 4,

$$V_m^* = \frac{0.74 M_w^*}{N_0 e} \quad (4)$$

where N_0 is Avogadro's number, M_w^* is the molecular weight of the species, and e is the density. The factor 0.74 is entered by assuming the species to be hexagonally close packed. Arbitrarily choosing the molecular weight to be that of the monomer, and using the well-known relation between the correlation time and T_1 given elsewhere,[4] values of T_1 of 0.71 s for neat 2-aminoethanol and 0.41 s for neat 3-aminopropanol can be derived. The corresponding experimental T_1's are ~0.65 s for the 2-amino compound and ~1.1 s for the 3-amino derivative. The model used, where the relaxation rate is a function only of the molecular volume and the macroscopic viscosity, thus gives a calculated value for 2-aminoethanol in good agreement with the experimentally determined T_1's. However, this is probably largely fortuitous in light of the approximations and assumptions used. Nevertheless the longer experimental T_1's for 3-aminopropanol may be explained by increased intramolecular association and/or increased internal motion. An increase of the chain length by one carbon atom should not influence the internal motion to a large extent, especially since no effects are observed by prolonging the chain any further. Also it is informative to notice that for 3-aminopropanol the overall motion is fastest in dilute chloroform solution, while the highest degree of motional freedom for 2-aminoethanol seems to be achieved in H_2O or DMSO. These trends are consistent with a model invoking extensive intermolecular association for 2-aminoethanol, producing a comparatively large effective radius r_I^* for the nominally smaller molecule. Thus we propose that the difference between the T_1's of 2-aminoethanol and the next few homologues mainly reflects differences in intermolecular aggregation, paralleling the results from infrared studies where it has been found that five-membered rings, formed by intramolecular hydrogen bonding,[3] are less favored.

If we continue to examine Table II, the T_1's listed reveal a number of interesting trends. Independent of the choice of solvent system, going from 3-aminopropanol to higher homologues the T_1's decrease along the chain as could be expected on a molecular weight or size basis. As mentioned earlier, in neat solution or in chloroform solution an increased degree of segmental motion is observed as a function of distance from the hydroxyl group. Note that even for a short chain molecule like 2-aminoethanol a significant and reproducible change is observed between the C-1 and C-2 carbons. These observations result from a more effective anchoring of the OH group, indicating that the OH-OH hydrogen bond competes efficiently with the OH-NH hydrogen bond.

In more dissociating media like H_2O and DMSO these monotonic trends disappear, suggesting some disruption of the aggregates. For the 6-amino compound an increase in the T_1 values is obtained on proceeding from the center of the molecule toward both chain ends. This supports a model in which these molecules tumble as open chain structures by analogy to the situation for a variety of linear aliphatic compounds.[6d,f,17,18] It is interesting to note that the anchoring of the polar sites in these solvents is insufficient to overcome the restriction of motions caused by the central bulk of the aliphatic chain. There is, however, some indication that for the 6-amino derivative in aqueous solution the anchoring of the amino end is more effective compared to the hydroxylic end. This is not observed in the other cases.

The influence on T_1's of varying concentration and solvent is most easily demonstrated by comparing the T_1 data for the 2-amino and 3-amino derivatives. Generally, by decreasing the solute concentration we observed an increased overall motion due to break-up in aggregates and change in macroscopic viscosity. It must be stated here that the magnitude of the T_1's

obtained in aqueous solution should not necessarily be directly compared with values in other media. This emerges from the fact that the observed T_1's in water solution can be affected by the presence of protonated species. Even internally this factor may be of some importance. However, based on the low basicity of these substances (pK_a(ethanolamine) = 9.44) we think that this contribution to the relaxation rate is of a minor influence ($\leq$10%) and that the constancy of the relaxation times going from a 2 to a 0.5 M solution mostly reflects the excellent dissociative properties of water.

Finally, the fact that the relaxation times for 2-aminoethanol and 3-aminopropanol are of a comparable magnitude under dilute dissociative conditions could possibly be explained by comparatively strong solute–solvent interactions in the 2-amino case, or by a less favorable conformation with regard to overall tumbling.

C. Variable Temperature T_1 Experiments. The dependence of T_1 on temperature has been obtained for the two-, three-, and four-carbon compounds and the relevant data are presented in Table III. Arrhenius plots of ln T_1 vs. the inverse absolute temperature (Figure 3) give a measure of the activation energy for the T_1 process, which is a function of the rotational reorientation due to both overall and internal motions. The E_a values obtained from these measurements are relatively large[7] as might be anticipated for associated systems where molecular reorientation involves disruption of hydrogen bonding. However, although differences in molecular aggregation for the three compounds are evident (vide supra) there are no variations in activation energy within experimental error, which can be attributed to such differences.

In an earlier study it was noted that in *n*-butyl alcohol a small systematic decrease in E_a along the carbon chain correlated with the increase in segmental motion for carbons further from the anchored (OH) end of the molecule. In the amino alcohol compounds changes in T_1 along the chain are still observable but considerably smaller than for *n*-butyl alcohol. Clearly the activation energy of the T_1 process is a much less sensitive probe of the extent of intermolecular association in these systems than might be expected.

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