Intramolecular Hydrogen Bonds. X.[1] Intramolecular Hydrogen Bonding in ω-*N*, *N*-Diethylaminoalkanols

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The intramolecular hydrogen bonding between tertiary amino-nitrogen and hydroxyl-hydrogen atoms has been investigated infrared-spectroscopically in several acyclic[2,3] and alicyclic systems.[4] The systems so examined were, however, confined to those which contain the amino group in the position 2 or 3 to the hydroxyl group. The spectral shifts of the bonded OH from the free OH frequencies, $\Delta\nu$, in the OH-to-N bonded systems are much greater than those in the corresponding OH-to-O bonded systems with similar geometries,[5-9] suggesting that the tertiary amino-nitrogen is more basic, or stronger as a proton acceptor, than the hydroxyl- or ether-oxygen.[2] In fact, thermodynamical investigations[3,10] of the formation of inter- and intra-molecular OH-to-N(tertiary) and OH-to-O bonds have shown that the enthalpies of the former are higher than those of the latter. From this information, and from the fact[6,8] that acyclic α, ω-alkane-diols and their monomethylethers capable of forming an intramolecular hydrogen bond are confined to those which contain at most four or five carbon atoms by which the terminal, oxygen-containing groups are separated, it was expected that acyclic 5-dialkylaminopentanols might also be internally bonded, forming an eight-membered ring. This expectation has now been justified through the measurements of the infrared OH-stretching spectra of the $(C_2H_5)_2N-(CH_2)_n-OH$ series, where n is a number from 2 to 6.

Table 1 summarizes the diethylaminoalkanols examined and the data of their OH spectra in dilute carbon tetrachloride solutions. The spectral data of 2- and 3-diethylaminoalkanols are essentially the same as those reported by Flett.[2] For each alkanol in which the n value is 5 or less, two bands independent of the concentrations, due to a free and to a bonded OH group, were observed, while for 6-diethylaminohexanol no absorption due to any bonded OH group was observed. The spectral shift of these alkanols increases in the same order: $2<3<5<4$, as that of the $MeO-(CH_2)_n-OH$[6] and $PhCHOH-(CH_2)_{n-1}-OH$ series.[8] The spectral shift is a measure of the strength of the hydrogen bond[5]; it also reflects the distance between proton-acceptor and proton-donor.[5] However, it does not obey the Badger-Bauer rule[11] with respect to the enthalpy of the intramolecular hydrogen bond formation, because, in this case, the enthalpy involves, apart from the energy of the hydrogen bond interaction, the energy of an increase or a decrease in further repulsive interactions between non-bonded atoms associated with the cyclic hydrogen bond formation.[7] On the other hand, as the table shows, the equilibrium constant (K) between the free and the bonded OH species decreases with the number of n in the same order: $2>3>4>5$, as that observed in the ω-methoxyalkanol series:[7] therefore, it seems to be related to the change in entropy, rather than to the change in enthalpy, resulting from the hydrogen bond formation, as observed in the latter series.

Experimental

***N*, *N*-Diethylaminoalkanols.** 2-Diethylaminoethanol was a commercial product, while the others were prepared from the corresponding haloalkanols[1] and diethylamine by a method similar to that used for the preparation of 2-diethylaminoethanol,[12] except for 5-diethylaminopentanol, which was obtained by the reaction of chloropentyl acetate with diethylamine, followed by hydrolysis.[13] All the alkanols were purified by redistillation in an atmosphere of nitrogen. Of

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TABLE 1. PHYSICAL CONSTANTS AND INFRARED DATA OF THE $(C_2H_5)_2N\text{-}(CH_2)_n\text{-}OH$ SERIES

n	Bp °C/mmHg	n_D^{20}	Molarity $\times 10^3$	ν_{OH} cm^{-1}	$\Delta\nu_{1/2}$ cm^{-1}	$\log I_0/I$	ε	K
2	69/27	1.4413	3.84	3642	30	0.041	56	15
				3474	140	0.27	25	
			5.86	3640	40	0.075	56	12
				3474	156	0.42	25	
3	85/20	1.4442	4.45	3640	30	0.13	56	4.7
				3280	210	0.82	74	
4	100/13	1.4483	2.93	3642	30	0.11	56	3.5
				3157	214	0.695	101	
5	114/14	1.4539	4.28	3640	30	0.65	56	0.11
				3224	240	0.21	166	
6	132/14	1.4549	3.27	3640	30	0.55	56	
	(Found:	N, 8.07%.	5.08	3641	30	0.89	58	
	Calcd:	N, 8.08%)						

these, 6-diethylaminohexanol has not hitherto been described, while the others are known substances. The physical constants of the latter agreed with those reported in the literature.

Measurement of Infrared Spectra. All the measurements were carried out under the same operating conditions at about 25°C by a method previously reported,[14] on a Perkin-Elmer 21 single-beam spectrophotometer equipped with a lithium fluoride prism. The cell used had an optical path 3 cm long. The concentrations were about 0.004 mol/l in carbon tetrachloride.

Determination of Equilibrium Constants. The constants were determined on the assumption that the molar extinction coefficient of the free OH band is constant throughout the present series. Namely, the absorbance (A_r) of the observed free OH band of 6-diethylaminohexanol in a particular concentration (C_r) was taken as the reference standard; on this basis, the absorbance (A) of the free OH band of each alkanol was transformed into the concentration of free OH groups (C_f) by the equation: $C_f = A \cdot C_r / A_r$. The subtraction of this concentration from the total concentration of the alkanol (C) gives the concentration of bonded OH groups (C_b). The equilibrium constant (K) is the ratio of C_b to C_f. The K value obtained in this manner is rather more reliable than that based on either the relative peak-intensity or the integrated-intensity ratio, both of which assume the same molar extinction coefficients in bonded and in free OH groups, especially when the spectral shift is very large as in the present case. In fact, the ε value of the bonded OH band in the table, which was obtained on the basis of the calculated concentration of bonded OH groups, varies between one-half and three times that of the free OH band.

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