Proton Magnetic Resonance Study of Monomer–Dimer Equilibrium in N–H Bonds

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THE chemical shift of N–H in n.m.r. spectra is affected by such factors as inter- and intramolecular association, temperature, and pH. In order to obtain the true chemical shift of the N–H monomer, a study was made of the N–H position at concentrations ranging from 0·4—0·005 mole fraction, using carbon tetrachloride as solvent. By extrapolation to infinite dilution, the δ-value for the N–H monomer is obtained. In aliphatic and alicyclic amine systems a straight line is obtained when mole fraction is plotted against the N–H chemical shift, δ.* For aromatic amines, the slope of the curve shows a sudden change to lower fields at low concentrations, possibly as a result of the known effect of dilution of an aromatic solute by an inert solvent.

The equilibrium constant may be obtained by assuming that the equilibrium is limited to dimers as found by Somers and Gutowsky[1] for phenols, or by comparison of theoretical and experimental curves as reported by Feeney[2] for amines. We prefer to calculate the monomer–dimer equilibrium from the shift of N–H "dimer" from the pyridine complex.

We have therefore measured the N–H chemical shift for each amine, using pyridine as a solvent and in concentrations of 0·5—0·005 mole fraction.

Because of the shift of the tetramethylsilane signal when a high concentration of an aromatic substance is present, a correction was applied by measuring the signals with respect to cyclohexane in a sealed capillary tube placed next to the n.m.r. tube. The observed shift was corrected for changes in magnetic susceptibility according to the relationship reported by Pople[3] and worked out in detail by Mathur.[4] The volume magnetic susceptibilities not found in the literature were calculated from the corresponding Pascal constants.

When the N–H shifts (in c./sec., from Me_4Si) are plotted against mole fraction, and the curve is

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* Values of δ are given in c./sec. from tetramethylsilane; measurements were made using a Varian A-60 spectrometer operating at 60 Mc./sec.

[1] B. G. Somers and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 1963, **85**, 3065.

[2] J. Feeney and L. H. Sutcliffe, *J. Chem. Soc.*, 1962, 1123.

[3] J. A. Pople, H. J. Bernstein, and W. G. Schneider, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959.

[4] R. Mathur, E. D. Becker, R. B. Bradley, and N. C. Li, *J. Phys. Chem.*, 1963, **67**, 2190.

extrapolated to infinite dilution, we obtain a value which represents the N–H "dimer". This "dimer" is really $>$N–H $\cdots$ NC_5H_5, since, at infinite dilution in pyridine as solvent, no amine–amine association would be possible. However, we believe that this value, corrected for changes in magnetic susceptibility, is the one which should be used for δ (N–H dimer), because it represents the shift of N–H associated with another nitrogen and it is the closest approximation obtainable experimentally. We feel that this approach is at least as convenient as others employing theoretical consideration of curve-shapes or assumptions that, at certain concentrations, only monomers and dimers are present.

From the expression derived by Shoolery[5] and the limiting slope of the curve, the equilibrium constants were found for each amine studied, and these values, together with the positions of the N–H monomer and N–H "dimer", are given in the Table.

TABLE

	δ (N–H mon.)	δ (N–H "dim.")	K	pK_a
Ethylenediamine	52·7	73·6	6·65	9·98
Dimethylamine	28·6	51·9	4·23	10·64
Piperidine	61·8	99·8	3·88	11·13
Pyrrolidine	76·2	124·2	1·04	11·27
m-Chloroaniline	216·7	317·7	0·52	3·32

The higher the K-value, the higher the degree of association in the dimer. As is evident from the Table, there is no simple relationship between K and basicity, which indicates that other factors such as amine angle, rotational-freedom restrictions on the dimer, and anisotropy might affect the value of K.

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[5] C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *J. Phys. Chem.*, 1956, **60**, 1311.