The N-H Stretching Absorption Band Intensities in Secondary Amides, Secondary Thioamides, and Anilides

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The intensities of the N–H stretching absorption bands of a number of *N*-methylamides, *N*-methylthioamides and anilides have been measured in a solution of carbon tetrachloride. It was observed that the intensities of the N–H stretching absorption bands of *N*-methylacetamide and *N*-methylpropionamide are considerably higher than those of the same band in the corresponding anilides. On the other hand, the intensity of the N–H stretching absorption band of *N*-methylformamide is of the same order as that of formanilide. The pattern of variation of the intensity of the N–H streching absorption bands in these compounds is similar to that of the C=O stretching absorption bands of the same compounds, but the variation in their frequencies is different. It was also observed that the intensities of the N–H stretching bands of *N*-methylthioamides are considerably higher and their frequencies are lower than those of the corresponding secondary amides.

Variations in the position and integrated absorption intensities of the carbonyl band in aldehydes, ketones, esters, and amides have received considerable attention.[1-8] They have been generally interpreted in terms of changes in resonance contribution or the variation in the interaction of the orbitals in these molecules.[7,8] Some authors[3,6] have taken the mesomeric, inductive, and steric effects as well as the environmental factors into consideration to account for the variation in the integrated intensities of the carbonyl band. Huggins and Pimentel[9] measured the intensities of OH and NH stretching absorption bands of methanol, phenol, and pyrrole and found that the intensity of the OH stretching band in phenol is considerably higher than that of methanol. Stone and Thompson[10] discussed the variation in frequencies and intensities of the OH stretching bands of phenols with the electron-withdrawing or electron-donating substituents. Elliott and Mason[11] have shown that the frequencies and the intensities of the N–H stretching bands, the HNH bond angle and the N–H bond dipole gradient increase in monocyclic *N*-heteroaromatic amines relative to the values for aniline. Russel and Thompson,[12] and Kreuger and Thompson[13] measured the intensities of several characteristic absorption bands including those of O–H and N–H stretching absorption bands. From the studies of the position of the N–H stretching absorption bands of anilides and thioanilides Suzuki *et al.*[14] discussed the nature of *cis* or *trans* structure of the molecules. The authors report in this paper the intensities of N–H stretching absorption bands of a number of secondary amides, secondary thioamides, and anilides and correlate the results with those of C=O stretching absorption bands of some of the same compounds measured by earlier workers.[8]

Experimental

The infrared spectra of the N–H stretching absorption bands of the amides and the anilides were recorded with Perkin Elmer Model 221 infrared spectrophotometer using matched quartz cells of 3 cm thickness. The gear combinations were so chosen as to spread the spectrum to 100 cm^{-1} = 10 cm^{-1}. The operating conditions of the spectrophotometer were: slit programme=947, gain=2.3, attenuator speed=1100, expansion=XI and scale factor 4. *N*-methylthioacetamide was synthesised. The rest of the chemicals used were of British Drug Houe and Eastman Organic Chemicals. They were purified by conventional methods and dried before use. The functional groups responsible for H bond in amides, anilides and thioamides are the N–H and the C=O or C=S bond and therefore very dilute solutions of these amides and anilides in solutions of CCl_4 were used so as to eliminate intermolecular association. This is indicated by the presence of only one absorption band in the region of 3450 cm^{-1} arising from the stretching vibration of free N–H group in all compounds except for formanilide wherein one observes two absorption bands with a difference of about 20 cm^{-1} as shown in Fig. 1. On the other hand, the N–H stretching absorption band in acetanilide and the *N*-methylthioamides is a single absorption band as shown in Figs. 2 and 3. The concentrations of the amides and the anilides chosen were such that Beer's Law holds as given in Fig. 4 by the linear relationship between the absorbance and the corresponding molar concentration.

A point by point measurement of the molecular extinction

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coefficient ε of the band was made at intervals of 5—10 cm^{-1} and plotted against ν in cm^{-1}. The area under the curve was measured for an interval of $\nu-\nu_m=60$ cm^{-1} on either side of the band maximum by planimeter. ν_m is the frequency at the maximum absorption. As there is some overlapping of the two N–H stretching absorption bands in formanilide (Fig. 1), the total area of the two bands has been obtained by drawing symmetrical curves with respect to the maximum absorption of each curve and then substracting the area common to both the absorption bands from the sum of the two areas. The intensity of the bands for each compound was measured at three to four concentrations and the average values were calculated. The halfband width of all these absorption bands is in the neighbourhood of 15 cm^{-1}. Wings correction was not applied.

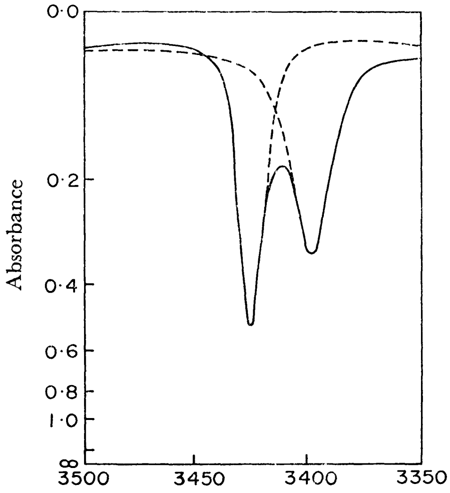

Fig. 1. N–H stretching band of formanilide in dilute solution of carbon tetrachloride. (Molar concentration = 0.0020)

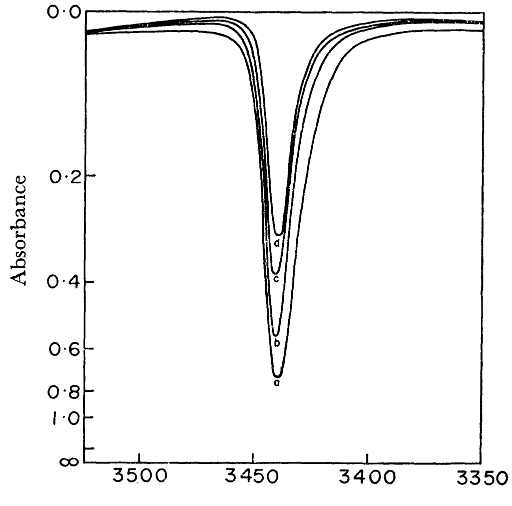

Fig. 2. N–H stretching band of acetanilide in dilute solutions of carbon tetrachloride at various concentrations.

(a) 0.0021 molar (b) 0.0015 molar
(c) 0.0010 molar (d) 0.0008 molar

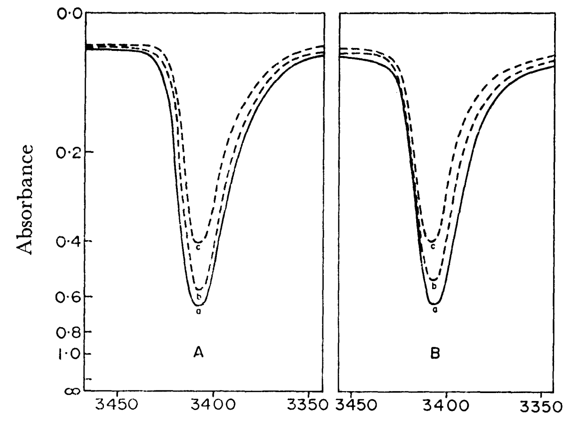

Fig. 3. A: N–H stretching band of *N*-methylthioacetamide in dilute solution of carbon tetrachloride at various concentrations.

(a) 0.0020 molar (b) 0.0015 molar (c) 0.0010 molar

B: N–H stretching band of *N*-methylthiopropionamide in dilute solution of carbon tetrachloride at various concentrations.

(a) 0.0020 molar (b) 0.0015 molar (c) 0.0010 molar

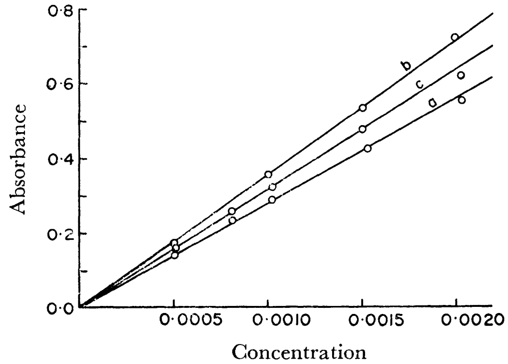

Fig. 4. Plot of absorbance *versus* molar concentration of:

(a) *N*-methylformamide
(b) *N*-methylacetamide
(c) *N*-methylpropionamide

Results

The intensities of the N–H stretching absorption bands of the secondary amides, secondary thioamides, and anilides measured in the solution of carbon tetrachloride are given in Table 1. The integrated intensities of the carbonyl band of some of these compounds obtained by the earlier workers[8] are also given in Table 1 for comparison. The existence of two bands in the N–H stretching region of formanilide is due to the co-existence of *trans* and *cis* structures because of the steric repulsion between the carbonyl group and phenyl group of *trans* form of formanilide. This makes the *trans* structure in formanilide less stable compared to that in the other anilides, since the steric repulsion is overcome by strong repulsion between the CH_3 group and the phenyl group in an anilide like acetanilide.

It is seen from Table 1 that as in the case of C=O stretching absorption bands, the intensities of the N–H stretching absorption bands of *N*-methylacetamide and *N*-methylpropionamide are higher than those of the corresponding anilides, whereas the intensity of the same band of *N*-methylformamide is of the same order as that of formanilide (in case of formanilide, the intensity given is the sum of the intesnsities of the N–H stretching absorptions of *trans* and *cis* structures). The result is similar to that obtained by the earlier workers[8]

TABLE 1. INTEGRATED INTENSITIES OF THE N–H AND C=O STRETCHING ABSORPTION BANDS IN SECONDARY AMIDES AND ANILIDES

Amide or anilide	N–H Stretching absorption band		C=O Stretching absorption band	
	Frequency	Intensity *A* (mol^{-1}·*l*·cm^{-2}×10^4 in solution of CCl$_4$)	Frequency	Integrated absorption intensity *A* (mol^{-1}·*l*·cm^{-2}×10^4 in solution of CCl$_4$)
N-Methylacetamide	3470	0.52	1691	3.5
Acetanilide	3440	0.42	1710	2.6
N-Methylpropionamide	3467	0.55	1688	3.6
Propionilide	3436	0.32	1701	2.4
N-Methylformamide	3460	0.55	1698	3.9
Formanilide	3420 3400	0.58	1704 (a doublet with a frequency difference of 5 cm^{-1})	4.0
N-Methylthioacetamide	3408	0.73	—	—
N-Methylthiopropionamide	3407	0.73	—	—

as regards the integrated intensities of the carbonyl band of the same compounds as shown in Table 1. The pattern of variation in intensities of N–H and C=O stretching bands of these compounds is similar, but it is different with respect to their frequencies. While the frequencies of the carbonyl bands of anilides are higher than those of the corresponding *N*-methylamides, the frequencies of the N–H stretching absorption bands of the same anilides are lower than those of the corresponding secondary amides. It is also seen from Table 1 that the intensities of the N–H stretching absorption bands of *N*-methylthioacetamide and *N*-methylthiopropionamide are considerably higher than those of *N*-methylacetamide and *N*-methylpropionamide. On the other hand, the frequencies of the N–H stretching absorption bands of the same secondary thioamides are lower than those of the corresponding ordinary secondary amides.

Discussion

In amides and anilides, no single valence bond structure is consistent with all their properties. Two possible structures contribute to the resonance hybrid in the molecules, with the dipolar resonance structure making substantial contribution to the ground state of the molecules giving partial single and double bond characters to the C=O and C–N linkages. Cannon[15,16] discussed this problem in terms of interaction and mixing of the π orbitals of C=O group and $2P_z$ orbitals of nitrogen atom in the sp^2 hybrid configuration. The π–p orbitals mixing lengthens the bond length of C=O and shortens that of C–N bond relative to the normal valence bond structure. This may explain the high values of the intensities of N–H stretching absorption bands of secondary amides and anilides compared to those of amines reported by Elliott and Mason.[11] The important factor responsible for the difference in the positions and intensities of the N–H stretching absorption bands of *N*-methylamides and anilides may be due to the delocalisation of the lone pair of electrons of the amino group over the aromatic nucleus of the anilides.

The C–N stretching frequencies of primary and tertiary amides and thioamides and the stretching frequencies of the amide III bands in secondary amides and secondary thioamides are given in Table 2.

TABLE 2

Amide	Mode of vibration and Frequencies (in cm^{-1})	
	Mode	(Frequency in cm^{-1})
Formamide	ν (C–N)	1309
Thioformamide	ν (C–N)	1325
N-Methylformamide	Amide III	1248
N-Methylthioformamide	Amide III	1297
N-Methlacetamide	Amide III	1300
N-Methylthioacetamide	Amide III	1360
Dimethylformamide	ν (C–N)	1502
Dimethylthioformamide	ν (C–N)	1540
Dimethylacetamide	ν (C–N)	1494
Dimethylthioacetamide	ν (C–N)	1510

As seen from Table 2, the C–N stretching frequencies of primary and tertiary thioamides are higher than those of the corresponding ordinary amides. Similarly the frequencies of the amide III band in secondary thioamides, to which the contribution of C–N stretch is considerable, have higher values than those in the corresponding secondary amides. The higher values of the C–N stretching frequencies in the thioamides may thus be due to (i) the difference in the contribution of various modes of vibrations to this absorption frequency and/or (ii) higher double bond character of the C–N bond with the dipolar resonance structure making greater contribution to the ground state of the molecules than in the case of ordinary amides. These factors may be responsible for the high values of the intensity of the N–H stretching absorption bands in *N*-methylthioamides.

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