

Intensities of Vibration Bands. Part VII. The NH Group.*

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The integrated band areas of the fundamental stretching vibration band of the NH group in a number of types of compound have been determined, in order to correlate the band intensities with structural characteristics and the polar properties of this group. It has been found that marked differences occur between compounds of different classes, and in particular the intensities are very low with dialkylamines.

As part of a more general study of the intensities of vibration bands of polyatomic molecules we have measured the band associated with the fundamental stretching mode of the NH group in a variety of compounds. It was desirable in the first instance to limit the considerations to one key band, and primary amines containing the NH₂ group were therefore not examined since this group gives rise to a pair of bands differing in relative intensity in different circumstances. The compounds chosen included secondary amines, anilides, urethanes, and heterocyclic structures, and the object was to correlate the structural characteristics with the values of the integrated band areas A , the extinction coefficients E_{\max} at the band peak, and the half band widths (band widths at half-peak optical density).

Two earlier sets of data are particularly relevant to our work. Bell (*J. Amer. Chem. Soc.*, 1925, **47**, 2192, 3039; 1926, **48**, 813, 818; 1927, **49**, 1837) measured the spectra of many amines in the liquid state, and in particular the bands near 3 μ of the NH and the CH group. There is little doubt that, with these compounds in the liquid state, hydrogen bonding of the NH group will occur, and Bell's results are therefore not strictly comparable with those for the free NH groups. Also, exact quantitative measures of the band intensities cannot be made from Bell's results. However, one important trend is noticeable in his data, namely, that in relation to the intensities of the CH bands, those of the NH groups in different molecules vary considerably. The strength of the NH band shows a general increase on passing from dialkylamines through the alkylanilines to diarylamines.

Wulf and Liddel (*J. Amer. Chem. Soc.*, 1935, **57**, 1464) measured the first overtone of the NH stretching mode and estimated band areas for amines, amides, and heterocyclic compounds containing this group. Their results again show significant variations of intensity from one compound to another, although at the time they suggested that the rough constancy of the band intensity might be used for approximate quantitative determination of the NH group. Some details of their work are discussed below.

Richards and Burton (*Trans. Faraday Soc.*, 1949, **45**, 874) determined the intensities of the NH fundamental stretching vibration band in methylaniline, ethylaniline, and diphenylamine. Although it is impossible to compare their results with ours on an absolute basis, there is rough agreement as regards the relative values for the different compounds.

EXPERIMENTAL

The substances were measured in dilute solution in carbon tetrachloride, although, as explained below, a few were also examined in the vapour phase. Each compound was purified by recrystallisation or fractional distillation. The spectra were recorded on a Perkin-Elmer 12C instrument with lithium fluoride prism, the calculated slit widths being about 10 cm.⁻¹ although the effective values were almost certainly rather greater than this. A quartz absorption cell 2.0 cm. thick was used. Several separate solutions of each compound were made up by weighing, and these were diluted as required. The concentrations generally used were in the region of 0.001M.

The apparent band areas $B' = \int \ln (T/T_0) \cdot dv$ were determined by graphical integration. In determining these band areas there is the well-known difficulty of deciding the width in cm.⁻¹ over which integration shall be made. In general, here the extent of the wings measured was

* Part VI, preceding paper.

about eight times the apparent half-band width. It is possible that the values determined may be a few per cent too low (see Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72). Some plots of B' against c were satisfactorily linear, but others showed curvature. An extrapolation was carried out by plotting B'/cl against cl , the intercept giving A , the true band intensity. It is noteworthy that the plots of B' against cl which show appreciable curvature are for molecules which have a small value of the half-band width. The method of determining band areas takes into account the possibility of unsymmetrical band contour, any "hot" bands being included.

The apparent extinction coefficients $E_{\text{max}}^a = (1/cl) \log (T/T_0)_{\text{max}}$ were also plotted as a function of cl , and a limiting value at $cl = 0$ was obtained by extrapolation. This value differs from E_{max}^t , the true molecular extinction coefficient, in that it depends upon the slit width used. The apparent half-band widths (width at half-peak optical density) $\Delta\nu_{\frac{1}{2}}$ were also measured. These could only be estimated to about 0.5 cm.^{-1} , and in most cases appeared to vary little with concentration, *i.e.*, with optical density.

A few measurements were made on the dialkylamines and pyrrole with a Perkin-Elmer 21 double-beam spectrometer, a rock-salt prism being used.

RESULTS AND DISCUSSION

Some typical results are shown in Figs. 1—4. The curvature of the plots of B' against cl might arise from several causes. One of these is the formation of hydrogen bonds between NH groups in different molecules. However, the concentrations used are very low and such association is unlikely. On the other hand, the deviation from linearity is most noticeable with those compounds in which the NH group may have a greater surplus positive charge on the hydrogen atom, such as the carbazoles. It is more probable, however, that the effect arises because the spectral slit widths used are in some cases a high fraction of the half band widths, which appear to be fairly small for the heterocyclic ring compounds and anilides.

The other important feature is the doubling of the NH bands with some compounds. The positions of these components (cm.^{-1}) are as follows (w = weak, m = medium, s = strong) :

Acetanilide	3400 (w)	3442 (s)	Formanilide	3408 (m)	3434 (m)
<i>p</i> -Bromoacetanilide	3400 (w)	3445 (s)	<i>N</i> -Benzylaniline	3419 (m)	3450 (m)
α -Phenylacetanilide	3415 (s)	3441 (w)	<i>N</i> -Phenyl- α -naphthyl-		
α -Phenylaceto- <i>p</i> -toluidide	3416 (s)	3442 (w)	amine	3417 (m)	3434 (m)

It is impossible to interpret either of the components with the anilides as being due to the harmonic of the carbonyl group fundamental, and it seems certain that both bands are connected with the NH group. The most probable explanation is that in all these cases rotational isomerism can occur, and the fact that there is a reversal of relative intensity between the components when a phenyl group is substituted in the acetyl group of anilides suggests that stereochemical considerations determine the preponderance of one form or the other. The total intensity of both bands has been taken as the measure of the NH group vibration, and if this is done all the results seem to fall into line.

The results are collected in the Table. As regards values of the intensity A , it can be seen that there are distinct groups. The alkylaryl- or diaryl-amines have values in the range 1.6—2.4, anilides and urethanes 2.7—3.9, and heterocyclic compounds 4.9—6.5. By contrast, the intensities for the dialkylamines are very much lower. The measurements were made in carbon tetrachloride, with which certain dialkylamines appear to undergo a slow chemical reaction, and there was consequently some suspicion that the apparent disappearance of the NH band was connected with this. The spectra of dimethylamine and diethylamine were therefore measured in the vapour phase, and compared with that of pyrrole vapour. Also, with the dialkylamines the intensity of the NH band is far smaller than that of the CH group bands, whereas the reverse is true for pyrrole. Rough measurement of the NH intensities in the vapour gave values agreeing with these found for the solution, but all the values for the dialkylamines must be regarded at present as approximate. There is in this case the possibility of some overlap with the much more intense CH bands. The weak nature of the NH band in the dialkylamines seems in agreement with Bell's results quoted above. Further, a similar result was found

by Marion, Ramsay, and Jones (*J. Amer. Chem. Soc.*, 1951, **73**, 305) when studying alkaloids containing a piperidine ring, although the band could be found with alkaloids containing indole nuclei or secondary amide groups. While the NH bands could not be found with solutions, they were detectable with the solid substances, where hydrogen bonds are formed and the polar character of the grouping will be affected. In this connexion

FIG. 1.

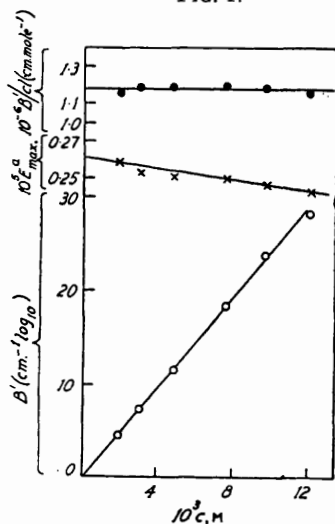


FIG. 2.

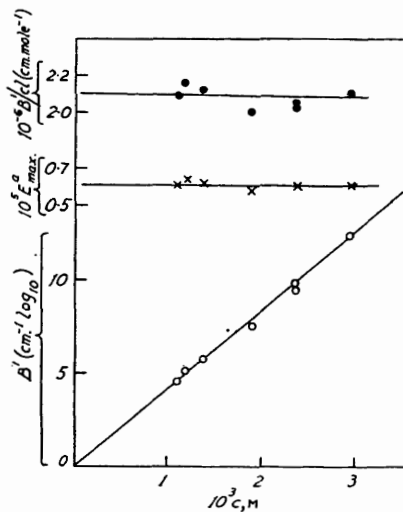


FIG. 3.

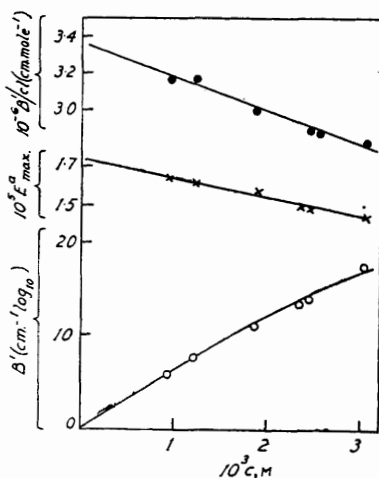
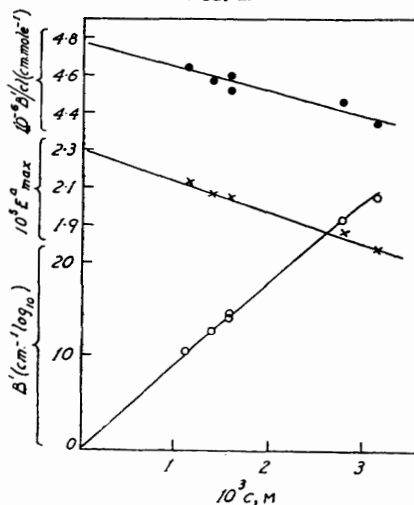


FIG. 4.



our result with 2-nitrodiphenylamine is significant. In this case there is internal hydrogen bonding of the NH group, and its vibration frequency falls to 3354. The band intensity is much higher than that for diphenylamine.

The extrapolated values of the extinction coefficients, namely $\text{Lt } E^a_{\text{max.}}$ follow roughly the same trend as the band areas, and also fall into fairly clear groups. There are obvious objections to their use for analysis and diagnosis, however, since they are far more dependent on spectrometer characteristics than the band areas, and the wide variation in half-band widths of the different types of compound complicates the position further. In addition, when doubling of the band occurs the extinction coefficient of one peak is only

partially significant. In the Table the values in parentheses for anilides refer to the predominant component of the band pair, but no values are given for formanilide, *N*-benzylaniline, or *N*-phenyl- α -naphthylamine where the components have about the same intensity.

The different classes of compound also have characteristically different NH band widths. This is a matter for further discussion when more results are available for other absorption bands.

ν and $\Delta\nu_{\frac{1}{2}}$ in cm.^{-1} .

Intensity $A = (1/cl) \int \ln(I_0/I) \cdot d\nu$ in $\text{cm.}^2 \text{ molecule}^{-1} \text{ sec.}^{-1}$.

Extinction coefficient $E_{\text{max.}} = \text{Lt}_{c \rightarrow 0} (1/cl) \log_{10} (T_0/T)_{\nu_{\text{max.}}}$ in $\text{cm.}^2 \text{ mole}^{-1}$.

Molecule	$10^3 A$	$\Delta\nu_{\frac{1}{2}}$	ν	$10^{-4} E_{\text{max.}}$
Dimethylamine	~0.5	—	~3350	—
Diethylamine	~0.5	~45	3334	—
Dipropylamine	~0.5	~45	3311	—
Dibutylamine	~0.5	—	3338	—
Piperidine	~1.0	—	~3350	—
Morpholine	~1.0	—	3351	—
Dibenzylamine	~3.0	—	~3330	—
<i>N</i> -Methylaniline	16	30	3433	3.9
<i>N</i> -Ethylaniline	13.6	35	3422	2.6
<i>N</i> -Benzylaniline	18.3	—	3419/3450	—
<i>N</i> -Phenyl- α -naphthylamine	18.4	—	3417/3434	—
Diphenylamine	22.2	25	3434	5.9
<i>N</i> -Phenyl- β -naphthylamine	24	27	3435	6.4
$\beta\beta$ -Dinaphthylamine	24	29	3434	6.1
Formanilide	27	—	3408/3434	—
Acetanilide	28	(15)	3400/3445	(12.5)
<i>p</i> -Bromoacetanilide	29	(14)	3400/3444	(13)
α -Phenylacetanilide	38	(14)	3416/3442	(14)
α -Phenylaceto- <i>p</i> -toluidide	37	(15)	3415/3441	(13.3)
<i>N</i> -Phenylurethane	39	14	3446	17
1-Methylcarbazole	49	19.5	3482	18
2-Phenylindole	49	19	3480	18
3-Methylcarbazole	55	16.5	3482	22.5
Carbazole	55	18.5	3478	23
Pyrrrole	57	14	3495	23.5
3-Methylindole	62	16.5	3490	25
Indole	65	14	3490	29
2-Nitrodiphenylamine	52	35	3354	10

We cannot at present use the values of the intensity A to derive quantitative measures of the polar properties of the NH bond. But the marked increase in A along the series shown in the Table suggests that $\delta\mu/\delta r$ for the NH bond is much greater in the heterocyclic bases than in simple dialkylamines. Chemical properties would suggest that the hydrogen atom in the ring compounds carries a greater positive charge than in the other compounds.

It seems likely that further important conclusions may be obtained by comparison of the intensities now measured with those of the NH overtone bands in these molecules. This should lead to information about the way in which the bond dipole varies with bond length (see Mecke, *Discuss. Faraday Soc.*, 1950, 9, 61; *J. Chem. Phys.*, 1952, 20, 1935). Rough comparisons with the data given by Wulf and Liddel (*loc. cit.*) for $2\nu_{\text{NH}}$ imply that the factor for alteration of intensity between ν_{NH} and $2\nu_{\text{NH}}$ is considerably different for the different classes of NH compound, as would be expected if the polar properties of their NH groups differ. It may be unwise to attempt quantitative calculations about this until the intensities for the overtones have been more carefully determined. The values given by Wulf and Liddel for the intensity of $2\nu_{\text{NH}}$ in dialkylamines are in marked contrast with those obtained by us for the fundamental, when compared with those for the other molecules, and the effect could only arise from a very significant difference in the nature of the NH bond in simple dialkylamines. Further work on this point is in progress.

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