Intensities of Vibration Bands. Part VIII. The C≡N Group.*

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The intensity of the stretching vibration band of the C≡N group has been determined in a number of compounds by measuring the integrated band areas, using solutions in carbon tetrachloride. The vibration frequencies, half-band widths, and extinction coefficients have also been determined. There are marked variations in the intensities which are related to structural features.

Investigations are now in progress on the intensities of vibrational absorption bands with the threefold purpose of obtaining values which may be used in quantitative analysis, of discovering further spectral characteristics for structural diagnosis, and of correlating the intensities with polar properties of specific bonds. In this paper, some results are given for the cyanide link. Kitson and Griffith (*Analyt. Chem.*, 1952, **24**, 334) and Cross and Rolfe (*Trans. Faraday Soc.*, 1951, **47**, 354) determined the apparent extinction coefficients of some nitriles. Their values fall into line with our own as regards relative magnitudes for the different compounds, but the absolute values depend upon the characteristics of the spectrometer used for measuring them. True integrated band areas which are less dependent upon the instrumental factors should be more generally useful, and should be more directly related to the molecular structural features.

Experimental

The spectrometer used was a Hilger D209 instrument, with calcium fluoride prism and modified for single-beam operation, the spectra being recorded automatically. Wave-length calibration was carried out with rotation lines of deuterium chloride (Pickworth and Thompson, *Proc. Roy. Soc.*, 1953, *A*, **218**, 37) and the lines of the water band at 6 μ. The effective slit widths were about 6 cm.$^{-1}$. Solutions of the cyanides in carbon tetrachloride were used, in rock-salt absorption cells. Three cells were used, of thickness 0·53, 0·74, and 2·37 mm., a choice being necessary for any given compound according to its solubility. The solutions were made up by weighing, concentrations lying in the range 0·2—1·1M. The cyanides used were commercial products purified by fractional recrystallisation, or refractionation under reduced pressure, sometimes in an atmosphere of nitrogen.

The band areas, B', given by $B' = \int \ln ({}_0T/T)_\nu \, . \, d\nu$, were determined by graphical integration, and the limiting values of B'/cl at $cl = 0$ were obtained. This involves an extrapolation which is sometimes not very satisfactory. In some cases, especially when the apparent half-band width is large, the plot of B' against cl is closely linear, and there is no difficulty. However, this plot is frequently curved. The curvature may be the result of errors in determining the band areas, but it is usually most marked with compounds for which the half-band width is small, and when the effective slit widths are a high fraction of the latter quantity. In such cases the extrapolation of the values of B'/cl at small values of cl involves uncertainty. The values obtained cannot at present be regarded as accurate to more than about $\pm 5\%$.

The apparent half-band widths, *i.e.*, width at half optical density, were also measured. Since only small changes were noticed over the range of concentrations studied, a mean value is given below, but this must be regarded only as an approximate indication of the true half-band width.

In some cases, the main band due to the cyanide group stretching vibration near 4·45 μ was overlapped by other weak bands. The latter were taken into account in measuring the intensities.

Results and Discussion

Table 1 summarises the values obtained. The compounds are seen to fall into fairly well-defined groups. The vibration frequency of the C≡N link in alkyl cyanides lies near 2250 cm.$^{-1}$, but conjugation with an aromatic ring, or the equivalent, lowers it to about 2230 cm.$^{-1}$. With the alkyl cyanides the intensities lie in the range 2·0—3·2 × 10^{-8}. All

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* Part VII, preceding paper.

the aromatic nitriles have much higher values which depend upon the nature and position of substituents in the aromatic rings. It may be noted that, although in acrylonitrile and α-methacrylonitrile the vibration frequency is roughly the same as those in the aromatic cyanides, yet the intensity of the band is low and of the same rough magnitude as those of the aliphatic cyanides. Values are given in Table 1 also for hydrogen cyanide and deuterium cyanide, measured in the vapour state by Hyde and Hornig (*J. Chem. Physics*, 1952, **20**, 647), and for cyanogen chloride (Nixon and Cross, *ibid.*, 1950, **18**, 1316). The intensity found for *p*-methoxybenzonitrile is particularly high, and it seemed possible that this might arise accidentally because of overlapping with some overtone or combination band of the methoxy-group; for several reasons this is now regarded as improbable.

Barrow (*ibid.*, 1953, **21**, 2008) has tried to correlate the band intensity of the carbonyl group in different compounds with its resonance energy, and has found a rough parallelism between A and the latter quantity; A is directly proportional to the quantity $(\delta\mu/\delta Q)$, the variation of molecular dipole moment with normal co-ordinate for the vibration. Values for the resonance energies of the cyanide link in some of the aromatic cyanides can be estimated as outlined by Wheland ("Theory of Resonance," Chapter 3, Wiley, New York, 1944) and by Barrow (*loc. cit.*). We thus obtain the results given in Table 2, and the plot shown in the Figure does in fact seem linear if the approximate nature of the values of the resonance energy is taken into account. For this purpose, it is assumed that the intensity in the gaseous phase is equal to that in carbon tetrachloride.

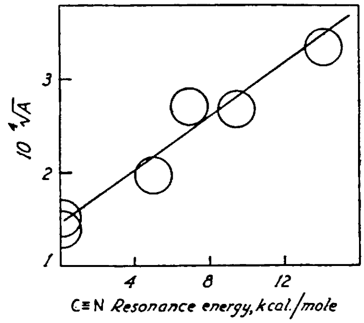

TABLE 1.

Values of $\Delta\nu_{\frac{1}{2}}$ and ν in cm.$^{-1}$. $A = (1/cl) . \int \ln (I_0/I)_\nu . d\nu$ in cm.^{2} molecule^{-1} sec.$^{-1}$.
$E_{\text{max.}} = (1/cl) \log_{10}) T_0/T)_{\nu_{\text{max.}}}$ extrapolated to $cl = 0$, in cm.^{2} mole^{-1}.

Compound	10^8A	$\Delta\nu^a_{\frac{1}{2}}$	ν	$10^{-4}E_{\text{max.}}$	Compound	10^8A	$\Delta\nu^a_{\frac{1}{2}}$	ν	$10^{-4}E_{\text{max.}}$
Methyl cyanide ...	2·1	10	2251	1·33	α-Naphthonitrile	7·4	9	2222	6·5
Ethyl cyanide	2·4	11	2247	1·65	β-Naphthonitrile	11·5	9	2227	9·5
n-Propyl cyanide ...	2·5	12	2250	1·6	3-Cyanopyridine	5·4	12	2231	3·4
n-Pentyl cyanide ...	3·2	14	2244	1·75	Acrylonitrile	2·0	14	2231	1·5
Benzyl cyanide ...	2·5	14	2251	1·2	α-Methacrylonitrile	2·3	10	2227	1·65
Diphenylacetonitrile	2·5	13·5	2244	1·3	Allyl cyanide	2·2	19	2250	0·85
Benzonitrile	4·1	10·5	2229	2·5	Ethyl cyanoacetate	2·1	18	2260	0·87
o-Toluonitrile	7·6	10	2226	5·3	Hydrogen cyanide	0·075	—	2089	—
m-Toluonitrile	7·7	8	2229	6·6	Deuterium cyanide	1·33	—	1921	—
p-Toluonitrile	10·2	8	2229	10·5	Cyanogen chloride	8·4	—	2214	—
p-Methoxybenzonitrile	18·4	9	2226	16·5					

TABLE 2.

Compound	Resonance energy (kcal /mole)	$10^4\sqrt{A}$	Compound	Resonance energy (kcal./mole)	$10^4\sqrt{A}$
Methyl cyanide ...	0	1·41	*o*-Toluonitrile	7	2·75
Ethyl cyanide	0	1·55	α-Naphthonitrile ...	9·5	2·71
Benzonitrile	5	2·0	β-Naphthonitrile ...	14	3·35

This preliminary survey suggests that it may be profitable to measure the band intensity for other substances containing the $C\equiv N$ link. The narrow nature of the band also implies that better quantitative results may result from the use of still smaller effective slit widths of the spectrometer.

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