

Alkyl Cyanates

IV. Infrared and Nuclear Magnetic Resonance Spectra

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The IR-spectra are shown of all the alkyl cyanates with C_1 – C_4 alkyls, except *tert*-butyl. The general shape of the IR-curves is discussed, and special emphasis is given to the complex band at *ca.* 2250 cm^{-1} .

Except for methyl cyanate the NMR proton spectra are likewise tabulated and discussed.

In the preceding paper¹ the preparation of alkyl cyanates $R-O-CN$, with C_1 to C_4 alkyl groups, except *tert*-butyl, has been described. Here we present a series of infrared and nuclear magnetic resonance spectra comparing and discussing characteristic features of the spectra of this new class of compounds.

INFRARED SPECTRA

The curves given on p. 444 ff. show the general appearance of the infrared spectra. Each spectrum was recorded several times using different samples of the same compound. The samples were prepared not only by thermolysis of alkoxythiazole, but also by decomposition of alkyl xanthogenamide with mercuric oxide.² Solutions (2 %) of the alkyl cyanates in carbon tetrachloride were used in recording the spectra.

Methyl cyanate rapidly isomerises and trimerises¹ whereas ethyl cyanate is transformed more slowly and the higher cyanates were unchanged after 20 h. In the dilute solutions, however, it was possible, even with methyl cyanate, to obtain spectral curves which do not show appreciable absorptions due to the decomposition products. The recording time was 10–40 min after which a duplicate spectrum was obtained.

All the spectra show very weak varying absorption in the range 3300 – 3400 cm^{-1} . This is assigned to the intense $N-H$ vibrations, presumably caused by hydrolysis. An absorption at *ca.* 1700 cm^{-1} appeared very weak

in the fresh solutions, but increased considerably on ageing. This is considered an impurity band and assigned to the isocyanate group, C=O vibration.

Some absorptions, however, showed considerable intensity variations, but never approached absorbance equal to zero. These bands may so be impurity bands which we are not able to remove by our methods, or they may be absorptions of the cyanates superposed on absorptions of some impurity. Such bands are marked with an arrow on the curves.

EXPERIMENTAL

Spectrometers used. Beckmann IR 9, 400–4000 cm^{-1} ; operated at a limit of resolution 0.5 cm^{-1} ; calibrated against NH_3 and CO_2 to an accuracy of $\pm 0.1 \text{ cm}^{-1}$.

Perkin-Elmer 21 B, 650–4000 cm^{-1} ; limit of resolution *ca.* 5 cm^{-1} .

Perkin-Elmer Infracord, 650–4000 cm^{-1} ; limit of resolution 6–8 cm^{-1} .

All instruments were operated as double-beam spectrometers using CCl_4 as reference. For this reason there may be some absorption bands in the region 730–820 cm^{-1} which have not been recorded because of the very intense absorption of the reference substance in this region; also the background appears with an appreciable absorption intensity in some of the spectra because the driving force of the pen is diminished when the reference signal is quenched.

Preparation of the solutions. Methyl cyanate was kept in the solid state at -80°C , at which temperature it could be stored for 24 h without appreciable decomposition. A solution was prepared from methyl cyanate melted by heating to -30°C and this was rapidly injected by means of a precooled micro syringe into carbon tetrachloride. The other esters were transferred to CCl_4 at room temperature immediately after distillation since previous experiments showed that no special precautions were necessary.

The spectral curves are reproduced from the Infracord spectra, whereas the discussion of frequencies and band structures etc. is based on the Beckmann IR 9 measurements.

DISCUSSION

The spectra show the expected CH stretching vibrations near 3000 cm^{-1} , the $\text{C}\equiv\text{N}$ stretching vibration at *ca.* 2250 cm^{-1} , and CH_3 and CH_2 deformations near 1460 and 1385 cm^{-1} .

Further the spectra show several intense deformational vibrations in the region 850–1500 cm^{-1} and some vibrations between 400 and 600 cm^{-1} , see Figs. 1–7 and Tables 1–3.

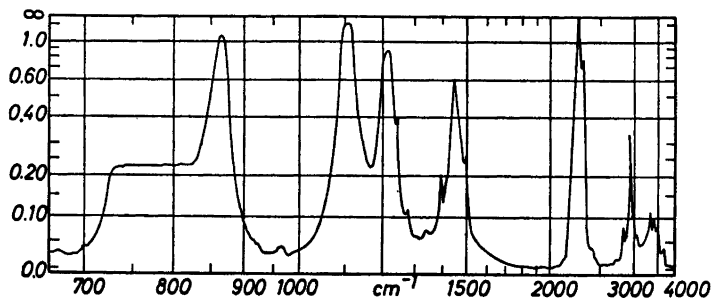


Fig. 1. Infrared spectrum of methyl cyanate.

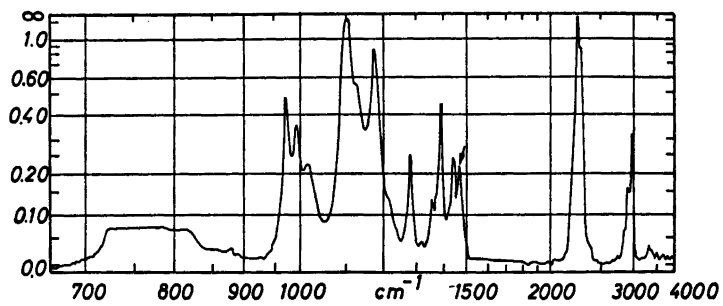


Fig. 2. Infrared spectrum of ethyl cyanate.

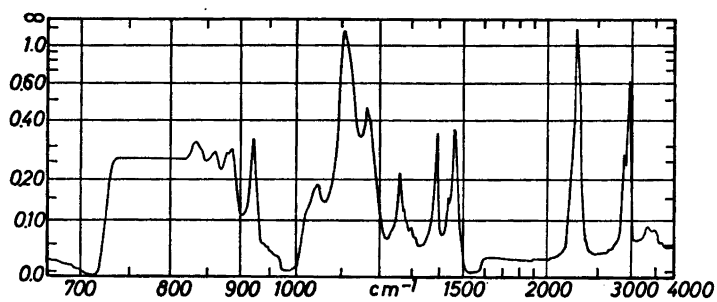


Fig. 3. Infrared spectrum of propyl cyanate.

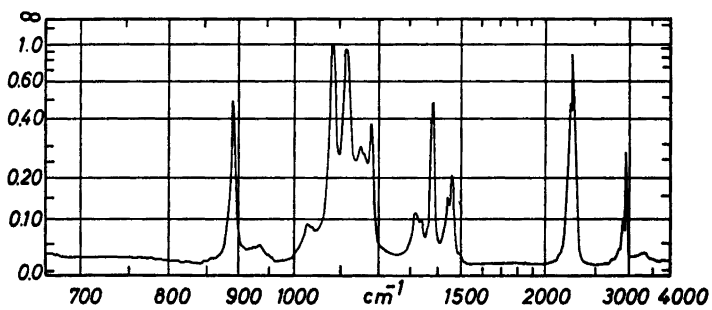


Fig. 4. Infrared spectrum of isopropyl cyanate.

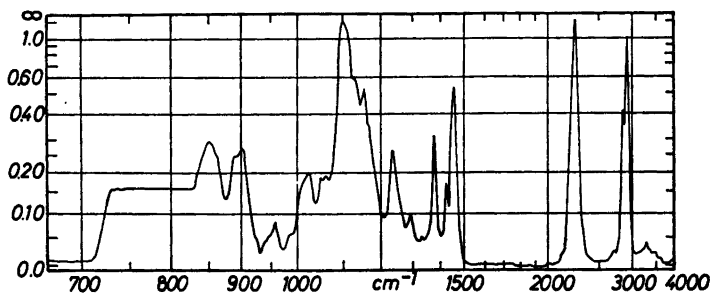


Fig. 5. Infrared spectrum of butyl cyanate.

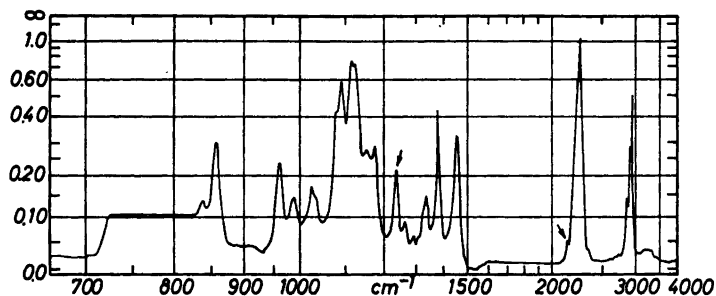
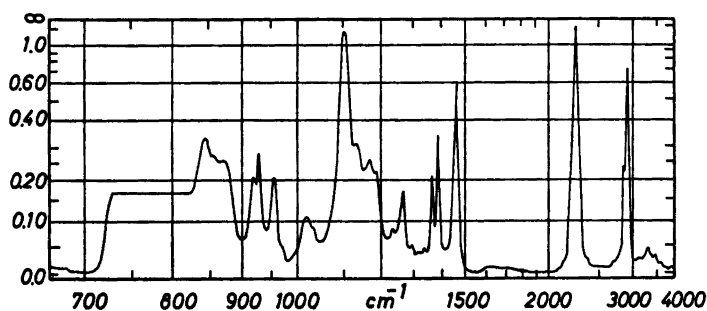
Fig. 6. Infrared spectrum of *sec*-butyl cyanate.

Fig. 7. Infrared spectrum of isobutyl cyanate.

The 1100 cm^{-1} frequency seems to be characteristic for the cyanates since it appears with high intensity in all the cyanate spectra, but is missing in the spectra of isocyanates.

It is generally assumed (*cf.* for example Bellamy³ and Katritzky⁴) that an alkyl C—O vibration in esters is to be found as an intense band in the range $800\text{--}1300\text{ cm}^{-1}$. So we will tentatively assign the 1100 cm^{-1} band in the cyanates to this vibration.

In the spectrum of isopropyl cyanate the 1100 cm^{-1} band seems to be split into two peaks of about equal heights (at 1084 cm^{-1} and 1123 cm^{-1}) and in the spectrum of *sec*-butyl isocyanate the intensity is distributed among

Table 1. Frequencies in the $400\text{--}650\text{ cm}^{-1}$ range of the infrared spectra of alkyl cyanates.

Compound	Frequencies (cm^{-1})	
Methyl cyanate	510 m	609 w
Ethyl cyanate	514 m	600 vw, broad
Propyl cyanate	458 vw	515 m
Isopropyl cyanate	460 vw	520 m
Butyl cyanate	515 m	631 w
<i>sec</i> -Butyl cyanate	520 m	575—620 w, diffuse
Isobutyl cyanate	518 m	

Table 2. Frequencies in the 1100 cm⁻¹ range of the infrared spectra of alkyl cyanates.

Compound	Frequencies (cm ⁻¹)	Compound	Frequencies (cm ⁻¹)
Methyl cyanate	1110 s sharp 1218 m broad	Butyl cyanate	1109 s sharp 1137 m shoulder 1162 m sharp
Ethyl cyanate	1102 s sharp 1127 w shoulder 1173 m sharp	<i>sec</i> -Butyl cyanate	1080 m sharp 1093 s sharp 1117 s sharp 1127 m shoulder 1167 m broad 1178 m sharp
Propyl cyanate	1107 s 1165 m	Isobutyl cyanate	1106 s sharp 1136 w 1169 m 1187 w
Isopropyl cyanate	1084 s sharp 1123 s sharp 1162 m broad 1185 m sharp		

Table 3. Structure of the 2250 cm⁻¹ band of alkyl cyanates.

Compound	Frequencies (cm ⁻¹)	Assignment	Difference
Methyl cyanate	<i>ca.</i> 2216 vw shoulder 2256 s sharp 2307 m shoulder	2 × 1110 fundamental 1110 + 1218	- 4 -21
Ethyl cyanate	2190 w shoulder 2245 s sharp 2278* m sharp	2 × 1102 fundamental 1102 + 1173 and/or impurity	-14 + 3
Propyl cyanate	<i>ca.</i> 2197 w shoulder 2247 s sharp 2266 m sharp	2 × 1107 fundamental 1107 + 1165	-17 - 6
Isopropyl cyanate	2202 vw shoulder 2226 m sharp 2255 s sharp 2282 w shoulder	1084 + 1123 fundamental 1123 + 1162	- 5 - 3
Butyl cyanate	2251 s sharp	fundamental	
the band shows weak diffuse increases of absorbance in the beginning and just after the maximum.			
<i>sec</i> -Butyl cyanate	2135* w sharp 2183 w shoulder 2225 m sharp 2255 s sharp	impurity ? 2 × 1093 2 × 1117 fundamental	- 3 - 9
Isobutyl cyanate	2211 w shoulder 2252 s sharp <i>ca.</i> 2276 w shoulder	2 × 1106 fundamental 1106 + 1169	- 1 + 1

* this band has shown varying intensity.

a peak at 1093 cm^{-1} and two peaks at 1117 cm^{-1} and 1127 cm^{-1} . It seems quite possible that two CH_3 groups or a CH_3 group and a C_2H_5 group, respectively, attached to the oxygen-bound carbon atom might give rise to a frequency splitting and an intensity distribution as observed here. The spectra of *sec*-butyl formate and *sec*-butyl acetate were found to show analogous intensity distribution in the same frequency range, but this was not the case with the corresponding isopropyl esters, so this question evidently needs further study.

The 2250 cm^{-1} band shows a complicated structure, *cf.* Table 3. The spectra of aryl cyanates^{5,6} also exhibit a splitting of the corresponding band. Because of the similarity of the characteristic frequencies of cyanates and isocyanates we investigated this band with special care. Since this spectral region is often empty we have a reasonable possibility of explaining the observed frequencies for each compound as *one* fundamental and some combination bands. We feel sure that the frequencies given in the tables are really cyanate frequencies, since the relative intensities did not vary with time and since an addition of isopropyl isocyanate and methyl isocyanate to the corresponding cyanates did not change the intensities of the weak shoulders, but only added new shoulders to the intense band.

In some cases (ethyl cyanate, isopropyl cyanate, and *sec*-butyl cyanate) a comparatively sharp peak remains to be explained. In the spectrum of *sec*-butyl cyanate the peak falls at distinctly lower frequency than the complex 2250 cm^{-1} band and we believe that it is due to some impurity in this compound. It does not change its intensity with time but the spectrum of one sample showed a definitely lower intensity.

In the case of ethyl cyanate we may possibly assign the 2278 cm^{-1} band to ethyl isocyanate. The ethyl cyanate was passed through a gaschromatograph immediately before recording the spectrum, but always the band appeared with the same intensity. In two runs, however, the compound was not purified gaschromatographically and here the 2278 cm^{-1} band showed a greater intensity. Addition of *ca.* 0.5 % ethyl isocyanate to the cyanate solutions simply added intensity to the 2278 cm^{-1} peak.

The IR-spectra of trialkyl cyanurates and trialkyl isocyanurates show no absorption band near 2250 cm^{-1} .

The molecules have only low symmetry (C_s or C_1) and so all fundamentals and all combination bands are allowed in the infrared spectra. Obviously the $1100\text{--}1200\text{ cm}^{-1}$ frequencies offer an explanation for the weaker absorption shoulders in the 2250 cm^{-1} band, although the assumed anharmonicity corrections show some variations (see Table 3). As seen from the tables it is possible to explain all the weak shoulders as combination bands or overtones of the frequencies in the $1100\text{--}1200\text{ cm}^{-1}$ range, but since we do not at present know the origins of the observed frequencies we cannot compare the combinations from one molecule with the combinations for the other molecules. On the other hand the number of strong bands in the $1100\text{--}1200\text{ cm}^{-1}$ range is not so great that we could always expect a combination to fit accidentally the shoulders and the medium intensity bands around 2250 cm^{-1} .

The low symmetry of the molecules gives ample possibilities for Fermi resonance but further spectroscopic data are needed before any conclusions can be drawn.

Since some interesting questions have arisen in the course of this investigation we are working to obtain further spectroscopic data, especially for methyl cyanate and isotopically substituted methyl cyanate so that a detailed analysis of the infrared spectra can be carried out.

NUCLEAR MAGNETIC RESONANCE SPECTRA

The proton magnetic resonance spectra of the above mentioned cyanates, except methyl cyanate, were obtained using a Varian A-60 instrument. The compounds were analysed as the pure liquids, using tetramethyl silane as internal standard. The spectra are tabulated in Table 4.

It is seen that the chemical shifts of the protons show the expected number of resonance bands, the expected integrated intensities, and that the observed multiplicity of each band agree with expectations according to the constitution. The intensities are normalized against the total number of protons in the molecule by adding the intensities of all the bands, dividing this intensity by the number of protons and using this quotient as divisor of the individual band intensities.

By comparing the NMR-spectra of ethyl cyanate with ethyl isocyanate, and of propyl cyanate with propyl isocyanate, it was found that the shifts

Table 4. Proton magnetic resonance spectra of alkyl cyanates.

Compound	Band centre, τ	Multiplicity, obs.	Normalized intensity	Explanation
Ethyl cyanate	5.46	4	1.9	$\text{CH}_2-\alpha$
	8.55	3	3.1	$\text{CH}_3-\beta$
Propyl cyanate	5.57	3	2.0	$\text{CH}_2-\alpha$
	8.15	12	2.0	$\text{CH}_2-\beta$
	9.00	3	3.0	$\text{CH}_3-\gamma$
Isopropyl cyanate	5.12	7	0.9	$\text{CH}-\alpha$
	8.52	2	6.1	two $\text{CH}_3-\beta$
Butyl cyanate	5.55	3	1.9	$\text{CH}_2-\alpha$
	8.20-8.65	very complex	4.0	$\text{CH}_2-\beta$ } overlapping
				$\text{CH}_2-\gamma$ }
	9.07	3	3.1	$\text{CH}_3-\delta$
<i>sec</i> -Butyl cyanate	5.33	6	0.9	$\text{CH}-\alpha$
	ca. 8.3	very complex	5.0	$\text{CH}_2-\beta$ } overlapping
	8.55	2		
	9.00	3	3.1	$\text{CH}_3-\gamma$
Isobutyl cyanate	5.72	2	1.9	$\text{CH}_2-\alpha$
	7.86	7	1.4	$\text{CH}-\beta$
	8.85	2	5.7	two $\text{CH}_3-\gamma$

of the α -protons were distinctly different in cyanates and in isocyanates, the cyanates being 1.17 ppm lower field. The β -protons of the cyanates similarly were 0.25 ppm lower field than the isocyanates.

A direct proof of the purity of the cyanate was obtained by adding 2 % propyl isocyanate to propyl cyanate. The proton signal appeared at the isocyanate frequency, having an intensity about 3 times the noise level, so we believe that the maximum contamination with isocyanate is less than 1 %.

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REFERENCES

1. Jensen, K. A., Due, M. and Holm, A. *Acta Chem. Scand.* **19** (1965) 438.
2. Jensen, K. A. and Holm, A. *Acta Chem. Scand.* **18** (1964) 2417.
3. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 2nd. Ed., Methuen, London 1960, p. 188.
4. Katritzky, A. R., Lagowski, J. M. and Beard, J. A. T. *Spectrochimica Acta* **16** (1960) 961.
5. Hoyer, H. *Chem. Ber.* **94** (1961) 1042.
6. Martin, D. *Chem. Ber.* **97** (1964) 2689.

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