

Infrared Spectra of Some Azido Derivatives of Methylpentopyranosides

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Eleven azido derivatives of methylpentopyranosides were studied by infrared spectroscopy in the 2100–2230 cm^{-1} region. The azido group absorption band was found to be split. Since no effect of the physical state of samples on the band splitting could be observed, this is ascribable to Fermi resonance. Other experimental data confirmed that the position of the azido group absorption band is associated with its stereochemical orientation in azido derivative molecule.

Azido compounds exhibit a strong absorption band as a result of the $-\overset{-}{\text{N}}=\overset{+}{\text{N}}=\overset{-}{\text{N}}$ asymmetric stretching vibration. The position of this band was earlier reported to be at 2141 cm^{-1} [1, 2], whereas in recent communications [3–7] a substantially broader range (2100–2170 cm^{-1}) for $\nu_{\text{as}}\text{N}_3$ of azido compounds is given.

The position of the absorption band is affected by substituents in the neighbourhood of azido group to a small extent only. However, the conjugation of the group results in shifting the band to higher frequencies by 20–40 cm^{-1} [4]. The intensity of the absorption band was found to be dependent upon electron releasing and withdrawing properties of substituents in the azido group environment [3]. The splitting of the absorption band corresponding to $\nu_{\text{as}}\text{N}_3$ has been explained by several authors as being due to Fermi resonance [5–7].

Azido derivatives of methylpentopyranosides have not been investigated by infrared spectroscopy. We selected this type of compounds in order to study the effects of some new factors (*e.g.* the conformation of azido group on the pyrane ring) on the $\nu_{\text{as}}\text{N}_3$ absorption band.

Experimental

All azido derivatives of methylpentopyranosides used in this study were prepared as described previously [8–10].

Infrared spectra were recorded with a double-beam UR-10 spectrometer (Zeiss, Jena). Each sample was measured using KBr technique (2 mg of compound in 1200 mg of potassium bromide). Spectra of samples No. 1, 2 and 4 were also measured in 4% chloroform solution in a sodium chloride cell of 0.11 mm thickness. Spectrum of sample No. 4 was recorded from Nujol mull as well (Fig. 1).

Results and Discussion

The characteristic frequencies are listed in Table 1. All azido derivatives of methylpentopyranosides showed a very intensive and split absorption band in the 2096—2160 cm^{-1} region resulting from the asymmetric stretching vibration of azido group (Fig. 1). As it may be seen from the results presented in Fig. 1 and Fig. 2 the physical state of the sample does not affect the splitting of the absorption band. This might be caused by Fermi resonance which is observed in systems with cumulative double bonds [5, 7].

The doublet observed in the 2100—2230 cm^{-1} region corresponds to the fundamental $\nu_{\text{as}}\text{N}_3$ vibration and to the ν_1 and ν_2 combination tone. The first component of the combination tone may occur in two types of vibrations with following positions of absorption band:

Table 1

Characteristic absorption frequencies in the infrared spectra of azido derivatives of methylpentopyranosides

No.	Compound	$\nu_{\text{as}}\text{N}_3$ [cm^{-1}]		$\nu_{\text{s}}\text{N}_3$ (ν_1) [cm^{-1}]	ν_{comb}	Conformation of pyrane ring	Steric orientation of N_3	Ref.
		$\nu_3 + \nu_2$ resp. $\nu_1 + \nu_2$						
1	Methyl-4-azido-4-deoxy- -2-O-mesyl-3-O-acetyl- β ,L- -arabinopyranoside	2105	2130	1235	1185(ν_3) 945(ν_2)	C 1	axial	[10]
2	Methyl-4-azido-4-deoxy- -2,3-di-O-mesyl- β ,L- -arabinopyranoside	2096	2140	1260	1185(ν_3) 950(ν_2)	C 1	axial	[8]
3	Methyl-4-azido-4-deoxy- - β ,L-xylopyranoside	2125	2210	1260	1260(ν_1) 950(ν_2)	1 C	equat.	[8]
4	Methyl-4-azido-4-deoxy- -2,3-di-O-mesyl- α ,L- -arabinopyranoside	2120	2160	1270	1190(ν_3) 965(ν_2)	C 1	axial	[9]
5	Methyl-4-azido-4-deoxy- -3-O-methyl- α ,L-xylo- pyranoside	2130	2230	1275	1275(ν_1) 950(ν_2)	1 C	equat.	[10]
6	Methyl-4-azido-4-deoxy- - α ,L-arabinopyranoside	2115	2160	1255	1170(ν_3) 985(ν_2)	C 1	axial	[10]
7	Methyl-4-azido-4-deoxy- - α ,L-xylopyranoside	2120	2230	1275	1275(ν_1) 945(ν_2)	1 C	equat.	[10]
8	Methyl-4-azido-4-deoxy- -2,3-di-O-mesyl- β ,D-xylo- pyranoside	2130	2210	1225	1225(ν_1) 985(ν_2)	C 1	equat.	[9]
	Methyl-4-azido-4-deoxy- -2,3-di-O-mesyl- α ,D-xylo- pyranoside	2135	2230	1265	1265(ν_1) 965(ν_2)	C 1	equat.	[9]
10	Methyl-4-azido-4-deoxy- -2,3-anhydro- α ,D-ribo- pyranoside	2100	2210	1250	1250(ν_1) 960(ν_2)	half-chair form	pseudo- equat.	[9]
11	Methyl-4-azido-4-deoxy- -2,3-O-benzoyl- α ,D-xylo- pyranoside	2110	2210	1260	1260(ν_1) 950(ν_2)	C 1	equat.	[10]

- a) C—N stretching vibration (ν_3) at 1170—1190 cm^{-1} ;
 b) N_3 symmetric stretching vibration (ν_1) at 1225—1275 cm^{-1} . The other one (ν_2) lying at 950—985 cm^{-1} could be attributed to C—C stretching vibration.

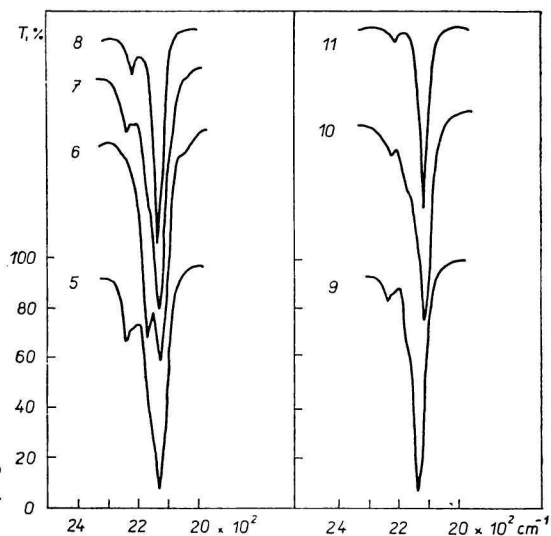


Fig. 1. Stretching vibrations of azido group in azido derivatives of methyl-pentopyranosides.

On the basis of experimental data shown in Table 1 it can be concluded that both substituents in the neighbourhood of azido group and the conformation of pyrane ring do not influence much the position of the $\nu_{\text{as}}\text{N}_3$ absorption band.

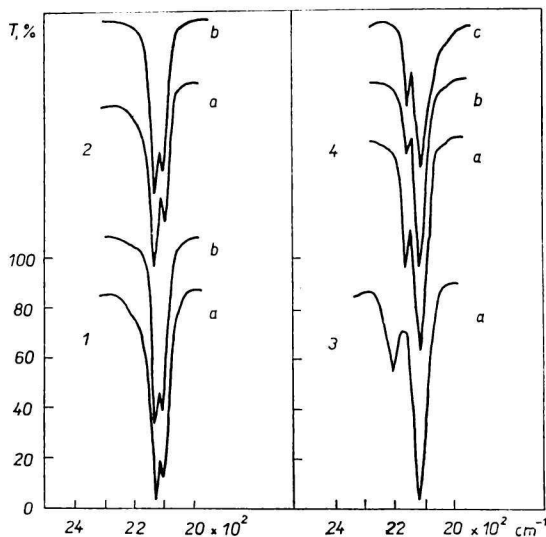


Fig. 2. Stretching vibrations of azido group in azido derivatives of methyl-pentopyranosides as measured in: a) potassium bromide; b) chloroform solution; c) Nujol mull. Samples No. 1—4.

On the other hand, the position of the absorption band (ν_{asN_3} and ν_{comb}) of the azido group of azido derivatives of methylpentopyranosides under investigation is decisively affected by its stereochemical arrangement on the pyrane ring. The absorption maximum of an axial azido group lies at 2130–2160 cm^{-1} , while that of an equatorial one lies at 2210–2230 cm^{-1} .

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