

Furan derivatives. XLVI. Infrared spectra of substituted 2-furyl cyanides

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The influence of substituents and solvents on the wavenumbers and integrated absorption intensities of the $\nu(\text{C}\equiv\text{N})$ bands of 5-substituted 2-furyl cyanides has been investigated.

Изучалось влияние заместителей и растворителей на волновые числа и интегрированные интенсивности полос поглощения $\nu(\text{C}\equiv\text{N})$ 5-замещенных 2-фурилцианидов.

According to [1–5], the wavenumbers of the $\nu(\text{C}\equiv\text{N})$ bands in the spectra of substituted phenyl cyanides are shifted towards higher values with respect to the wavenumber of phenyl cyanide [6–8] and this shift increases with increasing electron-acceptor character of the substituents. On the contrary, the integrated absorption intensities of these bands decrease with the increasing σ value of the substituent [9–12]. In some cases, owing to the presence of a strong electron-acceptor substituent no absorption was observed in the region of the stretching vibration of the $\text{C}\equiv\text{N}$ bond of the cyanide [13]. According to [7, 14] the $\nu(\text{C}\equiv\text{N})$ bands of cyanides are only slightly influenced by the nature of the solvent which would indicate that the $\text{C}\equiv\text{N}$ group does not interact *e.g.* with the hydrogen atom of chloroform. However, *Brown* [15, 16] and *Thompson* [9] have reported that integrated absorption intensities of the $\nu(\text{C}\equiv\text{N})$ bands of phenyl cyanides recorded in chloroform are higher than those in carbon tetrachloride.

In this work the evaluation of electron effects operating in 5-substituted 2-furyl cyanides is presented.

All studied cyanides display the $\nu(\text{C}\equiv\text{N})$ medium strong absorption bands in the region of 2231–2246 cm^{-1} . Similarly as with simpler cyanides [1, 2], the wavenumbers of the $\nu(\text{C}\equiv\text{N})$ bands of these compounds increase with the increasing electron-acceptor ability of the substituents, this being in a good agreement with the results reported by *Brown* [15] and *Thompson* [9]. The wavenumbers of the $\nu(\text{C}\equiv\text{N})$ bands of all substituted furyl cyanides were found to be higher than those of corresponding substituted phenyl cyanides [9]. Therefore, it may be assumed that the electron-acceptor power of the furan ring is stronger than that of the benzene ring. This assumption is in agreement with our results obtained previously [18, 19].

Integrated absorption intensities of the $\nu(\text{C}\equiv\text{N})$ bands of studied cyanides (Table 1) decrease with the electron-acceptor power of the substituents and they are influenced by the nature of the substituent as well as by the polarity of the solvent more significantly than the wavenumbers of the $\nu(\text{C}\equiv\text{N})$ bands. From spectral data of substituted 2-furyl cyanides it is evident that integrated adsorption intensities

Table 1

Spectral data of 5-substituted 2-furyl cyanides

Substituent	CCl ₄				CHCl ₃			
	$\tilde{\nu}$	$\Delta\nu_{1/2}$	ϵ^a	A	$\tilde{\nu}$	$\Delta\nu_{1/2}$	ϵ^a	A
CH ₃	2234	15	93	0.50	2231	17	137	0.85
H	2237	10	93	0.31	2236	11	145	0.56
Cl	2238	7	123	0.33	2237	9	168	0.56
Br	2237	10	111	0.39	2235	11	143	0.58
I	2238	9	98	0.30	2236	11	123	0.50
CH ₃ COO	2242	7	53	0.14	2243	10	71	0.24
NO ₂	2244	7	32	0.08	2246	9	51	0.16

$\tilde{\nu}$ and $\Delta\nu_{1/2}$ in cm^{-1} ; ϵ^a in $\text{l mol}^{-1} \text{cm}^{-1}$; $A = 2.303 \Delta\nu_{1/2} \epsilon^a K \times 10^{-4} \text{l mol}^{-1} \text{cm}^{-2}$.

of the $\nu(\text{C}\equiv\text{N})$ bands recorded for chloroform solutions are, similarly as with phenyl cyanides [9, 15, 16, 20], by 80% higher than those recorded for carbon tetrachloride solutions; *e.g.* for 5-nitro-2-furyl cyanide $A = 0.16 \times 10^4$ and $0.08 \times 10^4 \text{l mol}^{-1} \text{cm}^{-2}$ in CHCl_3 and CCl_4 , respectively. This fact may be explained by the interaction of the nitrogen atom of the $\text{C}\equiv\text{N}$ group with the hydrogen atom of chloroform.

Experimental

Infrared spectra of studied furyl cyanides were recorded with a double-beam Unicam SP 100 instrument in carbon tetrachloride and chloroform (concentration 0.1 \rightarrow 0.04 M, thickness of the cell 1.0 mm). The calibration was checked on the spectra of polystyrene and water vapour. Wavenumbers were determined with an accuracy of $\pm 1 \text{ cm}^{-1}$. Wavenumbers ($\tilde{\nu}$), half-band widths ($\Delta\nu_{1/2}$), apparent molar absorptivities (ϵ^a) are rounded to the nearest integer. Molar absorptivities were calculated by means of the base-line method and the true integrated absorption intensities from the relation: $A = 2.303 \Delta\nu_{1/2} \epsilon^a K \text{l mol}^{-1} \text{cm}^{-2}$. This relation could be used for the evaluation of integrated absorption intensities since the band contour follows the Lorentz function.

In the measurements, CCl_4 and CHCl_3 , anal. grade, were used. From chloroform, ethanol and moisture were removed by passing it several times through a column of blue silica gel. All investigated compounds were of anal. grade. The synthesis as well as the physical and chemical properties of these compounds excepting 5-iodo-2-furyl cyanide have been described in [17, 21]. 5-Iodo-2-furyl cyanide was prepared from 5-iodo-2-furaldehyde by the method described in [17] with a yield of 76%; m.p. of this compound was 78–80°C/4 torr.

For $\text{C}_5\text{H}_2\text{NOI}$ (218.99) calculated: 27.45% C, 0.91% H, 6.04% N; found: 27.52% C, 1.03% H, 6.35% N.

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