

Furan derivatives. CVI.

Infrared, ultraviolet, and Raman spectra of substituted 5-phenyl-2-furonitriles

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Received 2 November 1976

The influence of substituents and solvents on the wavenumbers and integrated absorption intensities of the $\nu(\text{C}\equiv\text{N})$ bands of substituted 5-phenyl-2-furonitriles has been investigated and their ultraviolet and Raman spectra are interpreted.

Исследовалось влияние заместителей и растворителей на частоты валентных колебаний и на интегральные интенсивности полос поглощения $\nu(\text{C}\equiv\text{N})$ замещенных 5-фенил-2-фулонитрилов и дана интерпретация их УФ спектров и спектров комбинационного рассеяния.

It is known that intensity and wavenumber of the $\nu(\text{C}\equiv\text{N})$ bands of nitriles depends on the nature of the substituents attached to the $\text{C}\equiv\text{N}$ group [1, 2]. Electron-releasing substituents cause the shift of the $\nu(\text{C}\equiv\text{N})$ bands to lower wavenumbers whereas electron-withdrawing ones to higher wavenumbers. The intensity of the $\nu(\text{C}\equiv\text{N})$ bands of nitriles is changing from very strong to undetectable. In this work we investigated the wavenumbers and integrated absorption intensities of the $\nu(\text{C}\equiv\text{N})$ bands and Raman and ultraviolet spectra of 5-phenyl-2-furonitriles. We focused our attention namely on evaluation of electrical effects and their transmission through the arylfuran grouping.

Experimental

Substituted 5-phenyl-2-furonitriles were prepared from appropriate furaldehydes through appropriate oximes [3—5].

Infrared spectra of compounds investigated were recorded with a Zeiss UR-20 instrument in the region of $2000\text{--}2300\text{ cm}^{-1}$ for chloroform and carbon tetrachloride solutions (concentration $2.5 \times 10^{-2}\text{ M}$, cell thickness 0.562 mm) as well as for KBr discs (2 mg/1 g

KBr). The calibration was checked against the spectrum of the polystyrene foil. The accuracy of the wavenumber reading was around $\pm 1 \text{ cm}^{-1}$. In the measurements, CHCl_3 , anal. grade, and CCl_4 , spectral grade, were used. Chloroform was freed from moisture and ethanol by passing it several times through a column of blue silica gel.

Raman spectra were recorded with a Spex Ramalog 4 instrument. A green line ($\lambda = 519 \text{ nm}$) of a Spectra Physics 164 argon ion laser was used to excite the compounds. The wavenumber calibration was checked against the spectrum of CCl_4 .

Ultraviolet spectra were recorded with a Zeiss UV VIS Specord instrument for dioxan solutions (concentration $2.5 \times 10^{-5} \text{ M}$, cell thickness 1 cm). The wavelength reading was around $\pm 1 \text{ nm}$.

Results and discussion

Infrared and Raman spectral data of compounds studied are listed in Table 1. In infrared spectra relatively intense bands are observed at $\sim 1030 \text{ cm}^{-1}$, corresponding to the bending vibrations of C—H bonds of the furan ring. In the Raman spectra only weak bands are observed in this region. The $\nu(\text{C}=\text{C})$ bands of the benzene ring are less marked in the infrared spectra of compounds investigated, however, these bands are the most intense in the Raman spectra. In the Raman spectra the $\nu(\text{C}\equiv\text{N})$ bands are marked. These bands are observed in the infrared spectra in the region of $2234\text{--}2225 \text{ cm}^{-1}$. Similarly, as with 5-substituted furonitriles [1] the wavenumbers of the $\nu(\text{C}\equiv\text{N})$ bands with substituted

Table 1

Infrared and Raman spectral data of substituted 5-phenyl-2-furonitriles

No.	X	Infrared		Raman	
		$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{C})$
I	4- CH_3O	2225	1614	2226	1612
II	4- CH_3	2227	1611	2228	1609
III	H	2231	1628	2234	1604
IV	4-Cl	2228	1606	2236	1604
V	4-Br	2234	1600	2235	1616
VI	2- NO_2	2233	1619	2231	1620
VII	3- NO_2	2228	1623	2230	1612
VIII	4- NO_2	2234	1606	2236	1600
IX	4- COOH	2233	1615	2236	1612
X	4- COOCH_3	2228	1612	—	1612

$\nu_s(\text{NO}_2)$ and $\nu_{as}(\text{NO}_2)$: IR, VI 1349, 1532, VII 1355, 1524, VIII 1351 and 1516 cm^{-1} ; R, VI 1349, VII 1353, VIII 1348 cm^{-1} .

$\nu_s(\text{CH}_3)$: IR, II 2917; R, II 2917 cm^{-1} (the most intense band in the spectrum).

5-phenyl-2-furonitriles increase with electron-withdrawing substituents and decrease with electron-releasing substituents, which is in accord with papers [5—8]. The wavenumber of the $\nu(\text{C}\equiv\text{N})$ of phenylfuronitrile (Table 1) was observed to be lower than that of 2-furonitrile [1] and nearly consistent with the wavenumber of benzonitrile [8].

From above mentioned, it appears that in consequence of the $-\text{M}$ effect of the $\text{C}\equiv\text{N}$ group the electron density on the $\text{C}\equiv\text{N}$ bond is decreased and therefore also a decrease of the wavenumbers of this bond is observed. Since the wavenumbers are lower with arylfuronitriles than those with corresponding furonitrile derivatives, one can assume that the electron-withdrawing power of the arylfuryl group is weaker than that of the furyl group and approximately equal to that of the phenyl group. Molar absorption coefficients and integrated absorption intensities decrease with electron-withdrawing substituents and increase with electron-releasing substituents and they are more influenced by the nature of the substituents as well as by the polarity of the solvents than the wavenumbers of the $\nu(\text{C}\equiv\text{N})$ bands of compounds studied (Table 2).

Integrated absorption intensities of the $\nu(\text{C}\equiv\text{N})$ bands with phenylfuronitriles are observed to be higher in all cases compared with appropriate furonitriles and approximately equal to those of appropriate benzonitriles.

A linear dependence of the $\nu(\text{C}\equiv\text{N})$ bands with 5-phenyl-2-furonitriles on δ constants has been found (Table 2; Fig. 1), $\rho = -0.1902$, $r = -0.9453$ (in CCl_4); $\rho = -0.1472$, $r = -0.9603$ (in CHCl_3).

Table 2

Infrared spectral data of the $\nu(\text{C}\equiv\text{N})$ bands of substituted 5-phenyl-2-furonitriles

No.	X	CCl_4				CHCl_3				σ
		$\tilde{\nu}$	$\Delta\nu_{1/2}$	ϵ	A	$\tilde{\nu}$	$\Delta\nu_{1/2}$	ϵ	A	
I	4- CH_3O	2229	9	208	0.66	2227	12	238	1.02	-0.27
II	4- CH_3	2230	9	180	0.57	2228	13	216	1.00	-0.07
III	H	2230	9	170	0.54	2231	12	201	0.86	0
IV	4-Cl	2232	9	165	0.52	2229	12	204	0.87	0.238
V	4-Br	2232	9	160	0.51	2234	13	203	0.84	0.265
VI	2- NO_2	2235	9	110	0.35	2234	11	150	0.59	—
VII	3- NO_2	—	—	—	—	2232	12	168	0.72	0.71
VIII	4- NO_2	—	—	—	—	2232	12	170	0.72	0.78
IX	4-COOH	2230 ^a	—	—	—	—	—	—	—	—
X	4-COOCH ₃	2228 ^a	—	—	—	—	—	—	—	—

a) Recorded for KBr discs.

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

Table 3

Ultraviolet spectral data of substituted 5-phenyl-2-furonitriles

No.	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$
I	214	4.49	304	4.58
II	214	4.52	296	4.55
III	214	4.10	294	4.47
IV	215	4.21	300	4.56
V	214	4.19	294	4.59
VI	214	4.54	266	4.31
VII	214	4.19	290	4.52
VIII	212	4.09	327	4.40
IX	214	4.44	307	4.61

 ϵ in $\text{l mol}^{-1} \text{ cm}^{-1}$.

2-Furonitrile (XI) $\lambda_{\max} = 242 \text{ nm}$ ($\log \epsilon = 4.06$); 5-bromo-2-furonitrile (XII) $\lambda_{\max} = 257 \text{ nm}$ ($\log \epsilon = 4.26$); 5-nitro-2-furonitrile (XIII) $\lambda_{\max} = 291 \text{ nm}$ ($\log \epsilon = 4.33$), $\lambda_{\max} = 215 \text{ nm}$ ($\log \epsilon = 4.43$).

Ultraviolet spectral data of compounds XI, XII, and XIII are included for comparison.

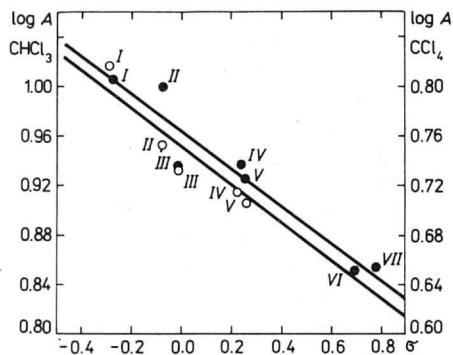


Fig. 1. Linear dependence of $\log A$ of the $\nu(\text{C}\equiv\text{N})$ bands on σ constants with substituted 5-phenyl-2-furonitriles.

● CHCl_3 ; ○ CCl_4 .

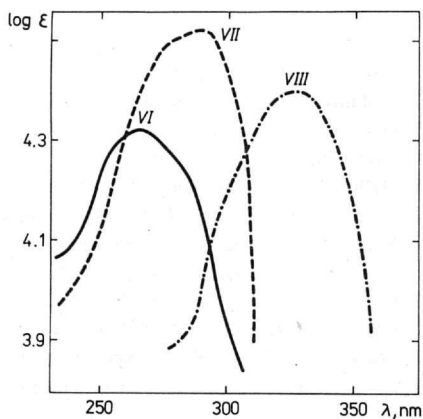


Fig. 2. Ultraviolet spectra of substituted 5-phenyl-2-furonitriles.

— 5-(2-Nitrophenyl)furonitrile;
 - - - 5-(3-nitrophenyl)-2-furonitrile;
 - · - · 5-(4-nitrophenyl)furonitrile.

Solvent: dioxan, $c = 2.5 \times 10^{-5} \text{ M}$, $d = 1 \text{ cm}$.

On passing from CCl_4 to CHCl_3 , integrated absorption intensities are significantly increased, which is connected with a change of the dipole moment during the vibration of the $\text{C}\equiv\text{N}$ bond after being influenced by the interaction with CHCl_3 .

Absorption maximum (Table 3) in the region of 290—330 nm (with the exception of 5-(2-nitrophenyl)-2-furonitrile) can be assigned to the whole conjugated system of the molecule. In the spectrum of 2-furonitrile an absorption maximum at 242 nm is observed. On substituting the hydrogen atom by the phenyl rest in position 5, a significant bathochromic shift (by 52 nm) is observed, which can be assigned to the prolongation of the conjugated system of the molecule. On replacing the phenyl group with 5-phenylfuronitrile by the 4-tolyl and 4-anizyl groups, respectively, a bathochromic shift of the absorption maximum is also observed (Table 3). Similarly, also with other derivatives a bathochromic shift of the absorption band in the region of 290—330 nm is observed. The absorption maximum in the u.v. spectrum of VI is significantly shifted to the shorter wavelengths compared with other derivatives thus indicating the shortened conjugated system. This can be only explained by the fact that in the case of 2-substituted arylfuran grouping in consequence of steric hindrances the benzene ring is twisted out of the plane of the furan ring (Fig. 2). These conclusions are in accord with previous papers [9—12].

References

1. Považanec, F., Piklerová, A., Kováč, J., and Kováč, Š., *Chem. Zvesti* **29**, 408 (1975).
2. Bellamy, L. J., *The Infrared Spectra of Complex Molecules*, p. 264. Methuen, London, 1964.
3. Považanec, F., Kováč, J., and Krutošíková, A., *Collect. Czech. Chem. Commun.* **41**, 1692 (1976).
4. Sherman, N. R. and Esch, A. V., *J. Med. Chem.* **8**, 25 (1965).
5. Hahn, W. E., Krajewicz, F., and Nowaczyk, M., *Lodž. Towarz. Nauk*, **III**, **6**, 15 (1960).
6. El Sayed, M. F. A., *J. Inorg. Nucl. Chem.* **10**, 168 (1958).
7. Krueger, P. J. and Thompson, H. W., *Proc. Roy. Soc.* **243A**, 143 (1957).
8. Cabana, H., Patenende, J. L., Sandorfy, C., and Bavin, P. M. G., *J. Phys. Chem.* **64**, 1941 (1960).
9. Frimm, R., Kováč, Š., Kováč, J., and Bencze, K., *Chem. Zvesti* **22**, 361 (1968).
10. Frimm, R., Kováč, Š., Kováč, J., and Bencze, K., *Chem. Zvesti* **22**, 447 (1968).
11. Frimm, R., *Thesis*. Slovak Technical University, p. 149. Bratislava, 1967.
12. Krutošíková, A., *Thesis*. Slovak Technical University, p. 90. Bratislava, 1970.

Translated by Š. Kováč