On Furan Derivatives. XVII.
Preparation and Infra-red Spectra of 5-Aminofuroates

[a]P. KRKOŠKA and [b]A. JURÁŠEK

[a]*Department of Chemical Technology of Wood, Cellulose and Paper* and
[b]*Department of Organic Chemistry, Slovak Technical University,*
Bratislava 1

Ethyl 5-aminofuroate and new-synthesized methyl, *n*-propyl and isopropyl esters thereof are assumed to exist in an amino form. This assumption is based upon the *Bellamy — Williams* correlation between $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ in the infra-red region of the spectrum. The effect of solvents different in polarity upon the vibration of characteristic groups of ethyl 5-aminofuroate was investigated.

Only a few free amino derivatives of furan have been reported. The preparation of free 2-aminofuran was so far unsuccesful [1—12]. The ring substituents of 2-aminofuran are of stabilizing effect upon the furan skeleton. *Marquis* [1] prepared ethyl 5-aminofuroate by reduction of ethyl 5-nitrofuroate with mercury(II) chloride activated aluminium in ethanol. This method was later modified by *Dann* [9] who performed the reduction in wet ethyl ether under an inert carbon dioxide atmosphere. *Frank* and co-workers [16] used this method for preparation of a series of amino derivatives.

Attempts to reduce ethyl 5-nitrofuroic acid with tin and hydrochloric acid resulted in failure. Succinic acid, ammonia and carbon dioxide were isolated from the reaction mixture [17]. The instability of furan amino derivatives is explained by the existence of an amino-imino tautomerism; it is assumed that the imino form is unstable and decomposition of amine occurs through imino form, the furan ring being opened [18]. The instability of ethyl 5-aminofuroic acid is rationalized similarly [17, 19—21].

To study the assumed amino-imino tautomerism, esters of 5-aminofuroic acid were synthesized (methyl, ethyl, *n*-propyl, isopropyl) and subjected to spectral study in infra-red region *Bellamy — Williams* correlation being used.

Experimental

Alkyl 5-nitrofuroates were synthesized according to [22]. Nitro group was reduced according to [9] with activated [23] aluminium. Melting points are uncorrected.

Preparation of 5-aminofuroates

0.2 mole of the particular 5-nitrofuroate dissolved in 2 l wet ether, was placed into a three-necked flask provided with a glass inlet tube. The flask was immersed into a cooling vessel with cold water and aluminium splinters (15 g) activated with $HgCl_2$ were added. Carbon dioxide was passed through the contents of the flask for 24 hours. Solid parts were then filtered off, washed three times with 100 ml ether on the filter funnel,

combined extracts were dried with Na_2SO_4, ether recovered up to $100-200$ ml and allowed to crystallize. 5-Aminofuroates are crystalline substances, white in colour, turning dark and becoming resinuos while standing in air.

Amines were purified with charcoal and crystallized from benzene—petrol.

Methyl 5-aminofuroate was obtained in 64% yield, m.p. 134°C.

For $C_6H_7NO_3$ (141.12) calculated: 51.06% C, 4.99% H, 9.92% N; found: 51.21% C, 4.84% H, 9.83% N.

Ethyl 5-aminofuroate, m.p. 96°C, reported [19] 96°C.

n-Propyl 5-aminofuroate, 59% yield, m.p. 37°C.

For $C_8H_{11}NO_3$ (169.17) calculated: 56.79% C, 6.55% H, 8.28% N; found 56.48% C, 6.48% H, 8.21% N.

Isopropyl 5-aminofuroate, 47% yield, m.p. $84-85$°C.

For $C_8H_{11}NO_3$ (169.17) calculated: 56.79% C, 6.55% H, 8.28% N; found: 56.62% C, 6.62% H, 8.17% N.

Spectral measurements

Infra-red spectra were taken with a UR-10 Zeiss spectrophotometer in $3600-800$ cm^{-1} region. 5-Aminofuroates (methyl, ethyl, n-propyl, isopropyl) were run in KBr cells 0.427 mm in width, concentration 0.025 м, solvent carbon tetrachloride.

The effect of solvent upon frequencies of characteristic ester groups was studied in NaCl cells 0.41 mm in width in 0.05 м concentration. Solvents were used as follows: carbon tetrachloride, chloroform, acetonitrile, trichloroacetonitrile and nitromethane.
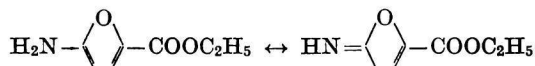
Results and Discussion

As known [24, 26] a correlation between frequencies $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ of aromatic and heteroaromatic amines in non-polar solutions (carbon tetrachloride) is given by the equation

$$\nu_s(NH_2) = 345.53 + 0.876\,\nu_{as}(NH_2).$$

Thus the problem of amino-imino tautomerism of some heterocyclic and aromatic system was investigated and using this equation it was ascertained that many derivatives being assumed to exist in an imino form, e.g. 2-aminopyridine [25, 27] 9-aminoacridine [26], derivatives of purine, triazole [27], exist in amino form.

The mentioned equation was applied to amino derivatives of furan where — the low stability being kept in mind — an imino-amino tautomerism is anticipated:

$$H_2N-\!\!\underset{}{\langle\!\!\!\overset{O}{}\!\!\!\rangle}\!\!-COOC_2H_5 \leftrightarrow HN=\!\!\underset{}{\langle\!\!\!\overset{O}{}\!\!\!\rangle}\!\!-COOC_2H_5$$

Characteristic vibrations of the investigated amino derivatives are listed in Table 1.

The study of spectral data of amines presented in this paper and the comparison of spectral data with those of the other amines where the amino-imino tautomerism was investigated shows that the existence of an amino-imino tautomerism so far presumed is not real enough.

All amines under study exhibited in carbon tetrachloride relatively intensive two absorption bands, stabile in location, the first of which at 3500 cm^{-1} corresponds

to $\nu_{as}(NH_2)$ and the second one at 3406 cm⁻¹ to $\nu_s(NH_2)$. The intensity and location of these bands is in good agreement with NH_2 group vibration of a series of typical amines [25, 28—30].

Table 1

Characteristic frequencies of 5-aminofuroates given in cm⁻¹

R	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\Delta\nu(NH_2)$	$\nu(C{=}O)$	$\delta(NH_2)$	$\nu(C{=}C)$	ν_f
Methyl	3500 w	3408 m	+3.5	1720 vs	1630 s	1593 w	1019 m
Ethyl	3500 w	3406 m	+5.5	1714 vs	1627 s	1594 w	1016 m
Isopropyl	3500 w	3406 m	+5.5	1968 vs	1625 vs	1593 w	1020 m

w = weak, m = medium, s = strong, vs = very strong.
ν_f = ring breathing mode.

The calculated value $\nu_s(NH)_2$ (3411.5 cm⁻¹) is in good accord with the obtained $\nu_s(NH_2)$ values (see Table 1). The fact that the studied amines are present in amino form is supported by the finding that no absorption bands in the 3400—3300 cm⁻¹ region, characteristic for absorption of imines [31] were observed. The effect of solvents different in polarity upon frequencies of characteristic groups of ethyl 5-aminofuroate is shown in Table 2. The $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ frequencies are markedly influenced by the increasing polarity of solvents. However, the calculated value $\nu_s(NH_2)$ is slightly different from this of the found one, namely in little polar solvents. The instability of amino derivatives of furan does not result from the amino-imino tautomerism as was explained before, but it is probably a general feature of furan derivatives determined by their structure.

Table 2

Bond frequencies of ethyl 5-aminofuroate in different solvents given in cm⁻¹

Solvent	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu(C{=}O)$	$\delta(NH_2)$	$\nu(C{=}C)$	ν_f	$\Delta\nu(NH_2)$
Carbon tetrachloride	3500 w	3406 m	1714 vs	1627 s	1594 vw	1016 m	+ 5.5
Chloroform	3500 w	3403 m	1709 vs	1627 s	1596 w	1016 m	+ 8.5
Nitromethane	3478 w	3382 m	1715 vs	—	—	1019 m	+ 10
Acetonitrile	3455 w	3359 m	1713 vs	1639 vs	1600 w	1020 m	+ 13.4
Trichloroacetonitrile	3487 w	3393 m	1715 vs 1700	1630 s	—	1030 m	+ 7

vw = very weak, w = weak, m = medium, s = strong, vs = very strong.
ν_f = ring breathing mode.

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Translated by Z. Votický