1,2-Bis[4-(α,α-dicyano-p-N,N-dimethylaminobenzyl)phenyl]-1,1,2,2-tetracyanoethane (VII). A mixture of 1 mmole of chloranil, 1 mmole of V, and 30 ml of acetonitrile was refluxed for 2 h, after which the precipitate was removed by filtration and recrystallized twice from acetonitrile with activated charcoal to give VII (27%) with mp 205°C (mp 203-204°C [5]).

Tetracyanoquinodimethane—3,7-dimethylphenothiazine Molecular Complex. Boiling solutions of equimolar amounts of TCQD and 3,7-dimethylphenothiazine in the minimum amount of acetonitrile were mixed, the mixture was cooled, and the precipitated black crystals were removed by filtration and dried to give a product with mp 225°C (dec.) in 98% yield. Found: C 72.3; H 3.9; N 16.3%. $C_{12}H_4N_4 \cdot C_{14}H_{13}NS$. Calculated: C 72.4; H 4.0; N 16.2%. The starting complex was isolated after it was refluxed for 10 h in acetonitrile or for 1 h in DMF.

LITERATURE CITED

1. B. P. Bespalov and E. V. Getmanova, Zh. Org. Khim., 16, 2358 (1980).
2. B. P. Bespalov, E. V. Getmanova, A. A. Pankratov, and V. V. Titov, Khim. Geterotsikl. Soedin., No. 12, 1633 (1976).
3. A. L. Mndzhoyan (editor), Syntheses of Heterocyclic Compounds [in Russian], No. 5, Izd. Akad. Nauk Armyansk. SSR (1960), p. 56.
4. D. S. Acker and W. R. Hertler, J. Am. Chem. Soc., 84, 3370 (1962).
5. B. P. Bespalov, Zh. Org. Khim., 16, 839 (1980).

ACID—BASE PROPERTIES OF 1,2,5-OXADIAZOLES.

2.* AMINOFURAZANS

I. V. Tselinskii, S. F. Mel'nikova,
and S. N. Vergizov

UDC 547.793.2:543.422.6

The behavior of 3-R-4-aminofurazans (R = NH_2, CH_3, OCH_3, N_3, COOH, and NO_2) in sulfuric acid solutions was studied by electronic and PMR spectroscopy. The constants of protonation ($pK_{\alpha BH^+}$) at the amino group and in the ring were calculated from the changes in the spectra. Dependences of the position of the absorption maxima corresponding to $\pi \to \pi^*$ transitions and the $pK_{\alpha BH^+}$ values and with the σ^0 substituent constants were found.

In order to predict the behavior of furazan derivatives in acid-catalyzed reactions by a spectrophotometric method we investigated the protonation of 3-substituted 4-aminofurazans and calculated the corresponding acidity constants.

The absorption maximum corresponding to a $\pi \to \pi^*$ transition in unsubstituted furazan lies in the "vacuum" UV region [2]. The introduction of an amino group, which is capable of conjugation with the ring, gives rise to a decrease in the energy of the transition (Table 1). A hypsochromic shift of the absorption band is observed as the electron-acceptor properties of the substituent in the 3 position increase; the position of the maximum correlates with the σ_m^0 substituent constants:

$$\nu \cdot 10^{-4}\ (\text{cm}^{-1}) = (4{,}02 \pm 0{,}05) + (0{,}80 \pm 0{,}12)\,\sigma_m^0$$
$$(n=5,\ r=0{,}967,\ s=0{,}02). \qquad (1)$$

Aminofurazancarboxylic acid deviates from the correlation; this is probably associated with the presence of an intramolecular hydrogen bond.

---

*See [1] for Communication 1.

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 321-324, March, 1981. Original article submitted March 4, 1980.

0009-3122/81/1703-0228$07.50

TABLE 1. UV Spectra of Unprotonated (I) and Mono- (II) and Diprotonated (III) 3-R-4-Aminofurazans[†]

Compound	R	I, λ_{max}, nm ($\log \varepsilon$) (water)	II		III	
			λ_{max}, nm ($\log \varepsilon$)	H_2SO_4, %	λ_{max}, nm ($\log \varepsilon$)	H_2SO_4, %
I	NH_2	253,5 (3,757)	255,5 (3,479)	55	—	
II	CH_3	246 (3,519)	210 (3,431) 246 (2,708)	60	209 (3,413) 246 (3,188)	86
III	OCH_3	243,5 (3,693)	232 (3,474)	66	246 (3,634)	90
IV	N_3	202,5 (3,592) 231 (3,435) 267.5 (3,740)	212 (3,556) 251 (3,706)	71	214 (3,571) 258 (3,708)	93
V	COOH	287[‡] (3,295)	212 (3,218) 271 (2,322)	82	212 (3,443) 271 (2,799)	95
VI	NH_3^+	—	205 (3,342) 258 (2,580)	86	—	
VII	NO_2	214 (3,872) 340 (3,253)	218 (3,735) 292 (2,634)	93	—	

[†] The absorption bands with λ_{max} 231 and 214 nm in the spectra of IV and VII, respectively, were assigned to a ring $\pi \rightarrow \pi^*$ transition; the λ_{max} bands at 202.5 and 267.5 nm in the spectrum of IV were assigned to electron transitions in the azide group [3], while the λ_{max} band at 340 nm in the spectrum of VII was assigned to the n–π^* transition of the nitro group.

[‡] In 25% sulfuric acid; λ_{max} in water (272.5 nm) corresponds to the dissociated acid.

TABLE 2. Parameters of the Regression Equations and $pK_{\alpha BH^+}$ Values of 3-R-4-Aminofurazans[†]

Compound	R		$\log I = aH_A + b$		$-pK_{\alpha BH^+}$	Analytical wavelength, nm
			|a|	|b|		
I	NH_2,	II	1,06±0,02	2,06±0,05	1,94±0,07	253,5
(VI)	NH_3^+,	II	1,50±0,02	5,91±0,07	3,94±0,09	253,5
			1,17±0,06	4,83±0,24	4,13±0,30	205
II	CH_3,	II	1,57±0,02	3,37±0,06	2,15±0,08	246
			1,17±0,03	2,69±0,08	2,30±0,11	210
			1,03±0,04	2,29±0,08	2,22±0,12	PMR[‡]
		III	0,93±0,01	4,59±0,07	4,94±0,08	246
III	OCH_3,	II	1,69±0,03	4,25±0,08	2,51±0,11	234
			1,60±0,03	3,97±0,06	2,48±0,09	244
			1,53±0,03	3,74±0,07	2,44±0,10	246
			0,88±0,06	2,23±0,14	2,54±0,20	PMR[‡]
		III	1,07±0,03	5,15±0,10	4,81±0,13	246
IV	N_3,	II	1,54±0,02	4,44±0,05	2,88±0,07	267,5
			1,45±0,04	4,17±0,10	2,88±0,14	251
		III	2,00±0,12	10,17±0,64	5,08±0,76	258
			1,43±0,06	7,35±0,30	5,14±0,36	267,5
V	COOH,	II	1,24±0,05	3,95±0,15	3,19±0,20	215
			1,46±0,01	4,68±0,04	3,21±0,05	271
			1,58±0,02	5,16±0,07	3,27±0,09	287
		III	1,34±0,12	7,17±0,66	5,34±0,78	271
VII	NO_2,	II	1,34±0,04	5,98±0,17	4,46±0,21	214
			1,27±0,05	5,59±0,15	4,40±0,20	218
			1,63±0,02	7,24±0,10	4,44±0,12	340

[†] In the case of slopes of the regression lines that differ considerably from unity the $pK_{\alpha BH^+}$ values were calculated at the half-neutralization points.

[‡] Determined by means of PMR spectroscopy from the change in the chemical shift of the protons of the methyl group.

In sulfuric acid solutions the dependence of the extinction coefficient on the acidity function has two sigmoid sections for most of the investigated compounds (the characteristic

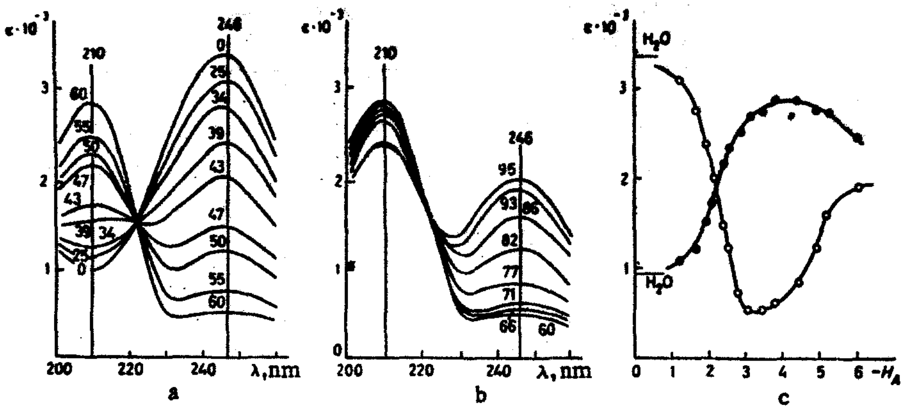


Fig. 1. UV spectra of 3-methyl-4-aminofurazan in sulfuric acid solutions (the concentration in percent is designated by the numbers on the curves): a) protonated at the amino group; b) protonated in the ring; c) dependence of the extinction coefficient on the analytical wavelengths 210 (●) and 246 nm (○) on acidity function H_A.

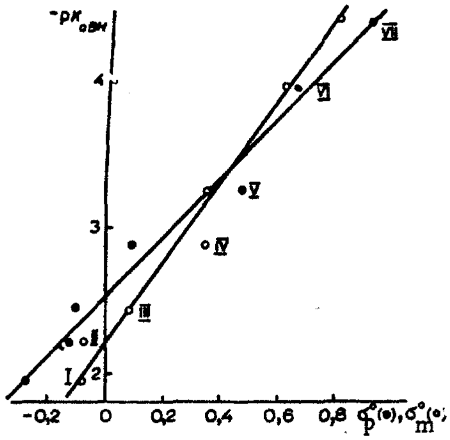
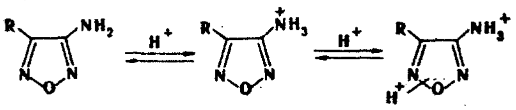


Fig. 2. Dependence of $pK_{\alpha BH^+}$ on the σ_p° and σ_m° substituent constants. The numbers of the points correspond to the numbers of the compounds in Table 1.

changes in the UV spectra in the case of 3-methyl-4-aminofurazan are presented in Fig. 1), and this indicates the existence of the following equilibria:



The characteristics of the UV spectra of unprotonated and protonated aminofurazans are presented in Table 1.

Protonation at the amino group reduces the absorption intensity; an absorption band of the protonated form appears in the short-wave region for most of the compounds in this case (Fig. 1a). Protonation in the ring has a slight effect on the absorption band of the protonated form, while the intensity of the long-wave band increases (Fig. 1b). Distinct isobestic points are not observed, particularly in the case of protonation in the ring. The analytical wavelengths were selected at the absorption maxima of the protonated and unprotonated forms of the compounds, and the effect of a change of solvent was not taken into account.

Aminofurazans are not Hammett bases, and the slopes of the regression lines in calculations with respect to acidity function H_0 are in most cases 0.55-0.70; we therefore used acidity function H_A, which best describes protonation in the ring [1].

TABLE 3. UV Spectra of 3-R-4-Aminofurazans in 30% Ethanol

Sulfuric acid concn., 10^3 g-eq / liter (− log N)	Extinction coefficients, liters-mole^{-1}-cm^{-1}			
	R−CH_3, λ_{max}−249 nm	R−C_6H_5		
		λ−212 nm (sh)	λ−231 nm (sh)	λ_{max}−270 nm
0	3250	4240	2690	3330
0,245 (3,61)	3320	4190	2730	3290
2,86 (2,54)	3280	4230	2690	3330
7,14 (2,15)	3330	4320	2740	3340
14,3 (1,85)	3330	4280	2760	3380
35,7 (1,45)	3380	4270	2730	3340
71,4 (1,15)	3280	4150	2650	3270

The pK_{aBH^+} values were calculated starting from the linear dependence of the logarithm of the ionization ratio on the acidity function by the method of least squares. The results are presented in Table 2.

The pK_{aBH^+} values for amine II determined by UV and PMR spectroscopy coincide within the limits of accuracy of the methods but are not in agreement with the values for this compound and a number of 3-phenyl-4-aminofurazan derivatives determined potentiometrically in 30% aqueous ethanol (the pK_s values range from 3.1 to 3.4 at 25°C) [4].

A study of the UV spectra of amine II and 3-phenyl-4-aminofurazan in 30% ethanol did not reveal substantial changes in the case of variation of the sulfuric acid concentration from 0 to 0.1 N (Table 3). The extinction coefficients at the absorption maxima are constant within the limits of the error in the method (±2%). A slight bathochromic shift (1-1.5 nm) is observed for II at 210-250 nm.

The pK_{aBH^+} values of the investigated aminofurazans correlate satisfactorily with the σ_m^0 and σ_p^0 substituent constants (Fig. 2):

$$pK_{a\,BH^+} = -(2{,}20 \pm 0{,}11) - (2{,}72 \pm 0{,}19)\sigma_m^0 \quad (n=7,\ r=0{,}988,\ s=0{,}059) \tag{2}$$

$$pK_{a\,BH^+} = -(2{,}55 \pm 0{,}12) - (2{,}04 \pm 0{,}13)\sigma_p^0 \quad (n=7,\ r=0{,}991,\ s=0{,}068) \tag{3}$$

To evaluate the mechanism of transmission of the effect of a substituent in the protonation of the amino group we correlated the pK_{aBH^+} values with σ_I^0 and σ_R^0 constants:

$$pK_{a\,BH^+} = -(1{,}98 \pm 0{,}33) - (3{,}17 \pm 0{,}83)\sigma_I^0 - (0{,}36 \pm 0{,}59)\sigma_R^0 \quad (n=7,\ r_{\text{set}}=0{,}92,\ s=0{,}448,\ r_I=0{,}88,\ r_R=0{,}30) \tag{4}$$

It is apparent from Eq. (4) that the coefficient of sensitivity of the pK_{aBH^+} values to the influence of the resonance effect differs insignificantly from zero. Thus the basically inductive nature of transmission of the substituent effect compels us to prefer Eq. (2) to Eq. (3), despite the somewhat smaller correlation coefficient.

A correlation between the position of the band of the $\pi \to \pi^*$ electron transition and the basicities of the compounds is observed for I-IV and VII:

$$pK_{a\,BH^+} = (11{,}5 \pm 1{,}4) - (3{,}40 \pm 0{,}33)\nu \cdot 10^{-4}\ (\text{cm}^{-1}) \quad (n=5,\ r=0{,}986,\ s=0{,}190). \tag{5}$$

Compound V again deviates from the correlation for the reason considered above.

The existence of a zwitterion structure for aminofurazancarboxylic acid is unlikely, since the pK_{aBH^+} value of this compound is calculated adequately from Eqs. (2) and (3) with the aid of the σ^0 constant of the carboxy group.

EXPERIMENTAL

The PMR spectra of solutions of II and III in sulfuric acid were measured with a Perkin–Elmer R-12 spectrometer (60 MHz) with tetramethylammonium bromide as the internal standard; the concentration was 90-100 mg/ml, and the temperature was 40°C. The UV spectra were measured with a Perkin–Elmer 402 spectrophotometer; the optical densities at the analytical wavelengths were recorded by means of a V2-23 digital voltmeter; the layer thickness was 1 cm, the concentration was $\sim 10^{-4}$ mole/liter, and the temperature was 25.0 ± 0.1°C.

The 25-90% sulfuric acid solutions were prepared as in [1].

A 100-120-mg sample of the investigated compound was weighed with an analytical balance and dissolved in distilled water in a 25-ml pycnometer. A 3-ml sample of sulfuric acid was placed in the cuvette by means of a buret and stirred and thermostatted at 25 ± 0.1°C for 4-5 min, after which the spectrum was recorded. The next portion of the solution was then added, and the procedure described above was repeated four to five times (until an optical density of 0.8 to 1.0 at the analytical wavelength was reached).

The extinction coefficient was calculated with allowance for the change in the concentration and volume of the solution due to the water introduced with the sample of the substance.

LITERATURE CITED

1. I. V. Tselinskii, S. F. Mel'nikova, S. N. Vergizov, and G. M. Frolova, Khim. Geterotsikl. Soedin., No. 1, 35 (1981).
2. R. A. Olofson and J. S. Michelman, J. Org. Chem., 30, 1854 (1965).
3. J. E. Gurst, in: The Chemistry of the Azido Group, S. Patai, ed., Interscience, New York–London (1971), p. 191.
4. G. Westphal and R. Schmidt, J. Prakt. Chem., 315, 791 (1973).

NITRO DERIVATIVES OF THE THIOPHENE SERIES.

2.* NITRATION OF THIENYL-SUBSTITUTED UNSATURATED METHYL KETONES

Yu. D. Churkin, L. V. Panfilova,
A. S. Shashkov, and K. Ya. Burshtein

UDC 547.732

The nitration of 4-(5-R-2-thienyl)-3-buten-2-ones with nitric acid in acetic anhydride is accompanied by the formation of a mixture of nitro isomers, whereas nitration with nitric acid and copper and aluminum nitrates in carbon tetrachloride, dichloroethane, and acetonitrile leads to the production of only the α-nitro ketone. The results of quantum-chemical calculations of the reactivity indexes within the CNDO/2 approximation are in agreement with the experimental data on electrophilic substitution of these compounds in the basic and protonated forms.

The nitration of thienyl-substituted α,β-unsaturated methyl ketones is possible via two pathways — in the heterocyclic ring and in the aliphatic chain [1]. To explain this it seemed of interest to make a detailed study of the reactivities of thiophene compounds that contain conjugated C=C and C=O bonds.

We calculated the electronic structure for 4-(2-thienyl)-3-buten-2-one (I) (within the CNDO/2 approximation on an s- and p-orbital basis without allowance for the d AO of sulfur by the method proposed in [2, 3]) and found the reactivity indexes of the molecule (the residual π-electron densities) for electrophilic substitution reactions (Fig. 1). We used the experimental geometry of ketone Ia in the calculations [1]. It follows from the data obtained that the probable reaction centers in ketone I are the 7, 3, 4, and 5 positions ($7 > 5 > 3 \approx 4$).

---

*See [1] for Communication 1.

V. V. Kuibyshev Polytechnic Institute, Kuibyshev 443645. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 325-328, March, 1981. Original article submitted March 20, 1980.

0009-3122/81/1703-0232$07.50