vestigated compound, and, on the basis of IR spectroscopic data, make it possible to form a judgment regarding the structures of the barbituric acids in solutions.

## EXPERIMENTAL

The calculations were made with a Minsk-22 computer with programs composed by L. A. Gribov and co-workers [7]. The IR spectra were recorded with IKS-14A and Perkin-Elmer 457 spectrometers. The spectra were obtained from suspensions of crystalline samples in mineral oil and perfluorinated oil on KBr plates. The spectra of solutions of the compounds were recorded in CaF$_2$ cuvettes.

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# FORMAZANS OF THE PYRIMIDINE SERIES

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UDC 547.556.9'854.3

A series of 1-(2'-pyrimidyl)-3,5-diarylformazans was synthesized. Their structures were studied by means of IR and electronic spectroscopy, and assumptions regarding the most probable tautomeric forms of the investigated compounds were made. The ionization constants of the formazans were measured. It was found that 2,5-diphenyltetrazoles are formed instead of the expected tetrazolium salts in the reaction of 1-(2'-pyrimidyl)-3,5-diphenylformazans with N-bromosuccinimide.

Of the formazans of the pyrimidine series, 3-uracilyl-1,5-diphenylformazans are known. A series of 1-(2'-pyrimidyl)-3,5-diphenylformazans (I-VIII, Table 1) was synthesized in order to study the effect on the structures and properties of foramazans of a pyrimidine residue in the 1 position as compared with aryl and benzazole fragments. These compounds were obtained from 2-hydrazinopyrimidines [2] by coupling of the arenediazonium salts with benzaldehyde 2-pyrimidylhydrazones [3] in alcoholic alkali.

The tautomerism of these formazans envisages a large number of possible forms, and the most probable such forms are presented in the scheme below.

One distinct and intense absorption band at 3384-3390 cm$^{-1}$ (Table 1), which can be assigned to the stretching vibrations of both the N—H bond and the O—H bond, is observed in the IR spectra of formazans I-V. In a comparison of the IR spectra of 1-(6'-methyl-4'-hydroxy-2'-pyrimidyl)-3,5-diphenylformazan (I) and 1-(6'-methyl-2'-pyrimidyl)-3,5-diphenylformazan (VII) at 1400-1700 cm$^{-1}$ it was observed that the spectrum of I contains a $\nu_{C=O}$ absorption band at 1665 cm$^{-1}$, which is absent in the case of formazan VII. This proves the presence of a keto group in the 4 position of the pyrimidine ring of I-V and suggests that

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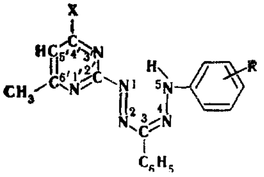
TABLE 1. Spectral Characteristics of Formazans



| Compound | X | R | $\nu_{NH}$, cm$^{-1}$ CCl$_4$ | $\lambda_{max}$, nm (lg ε) | | | | | | p$K_a$† |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | CCl$_4$ | benzene | acetone | alcohol | alcoholic NaOH | formazan complexes with Ni$^{2+}$ | |
| I* | OH | H | 3387 | 456<br>(4,05) | 455<br>(4,06) | 412<br>(4,04) | 405<br>(4,09) | 460 | 560 | 8,50 |
| II | OH | $p$-CH$_3$ | 3385 | 456<br>(4,06) | 455<br>(4,15) | 415<br>(4,07) | 409<br>(4,12) | 453 | 580 | 8,86 |
| III | OH | $o$-CH$_3$ | 3384 | 458<br>(4,08) | 461<br>(4,13) | 420<br>(4,05) | 404<br>(4,14) | 445 | 550 | 8,88 |
| IV | OH | $p$-NO$_2$ | 3387 | 490<br>(3,94) | 480<br>(4,07) | 444<br>(4,14) | 442<br>(4,20) | 530<br>580 | 606 | 8,28<br>12,83 |
| V | OH | $o$-NO$_2$ | 3390 | 467<br>(3,64) | 478<br>(3,76) | 423<br>(3,76) | 420<br>(3,98) | 490<br>520 | 590 | 8,55<br>13,60 |
| VI | OCH$_3$ | H | 3358 | 470<br>(4,09) | 468<br>(4,06) | 460<br>(4,09) | 458<br>(3,93) | 506 | 600 | 13,32 |
| VII | H | H | 3360 | 466<br>(4,09) | 468<br>(4,09) | 460<br>(4,07) | 464<br>(3,98) | 508 | 610 | 13,14 |
| VIII | OCH$_3$ | $p$-NO$_2$ | 3334 | 496<br>(3,88) | 488<br>(3,86) | 475<br>(3,80) | 470<br>(3,79) | 574 | 630 | 12,10 |

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* For a CCl$_4$ solution of this compound, $\nu_{C=O}$ is found at 1665 cm$^{-1}$.

† The pK$_a$ values were measured with an accuracy of ±0.08.

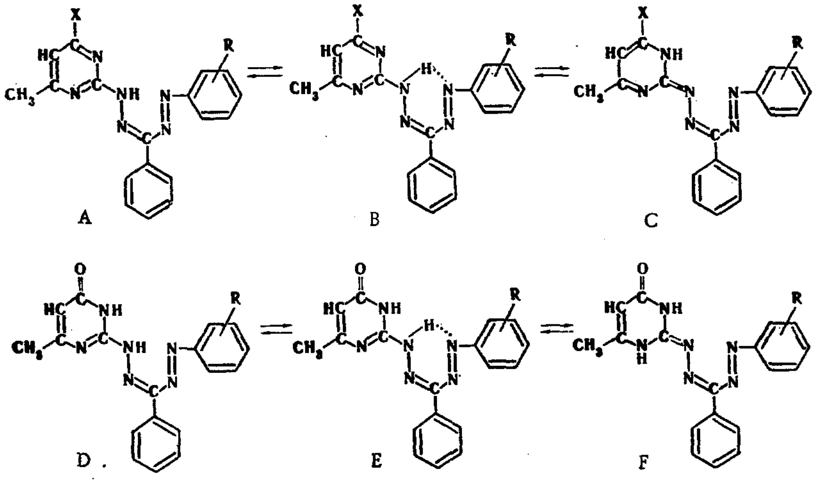
TABLE 2. Characteristics of the Compounds Obtained

| Compound | mp, °C | Empirical formula | Found, % | | | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | C | H | N |
| I | 188—189 | $C_{18}H_{16}N_6O$ | 65,4 | 5,0 | — | 65,0 | 4,9 | — |
| II | 214—215 | $C_{19}H_{18}N_6O$ | 66,0 | 5,2 | 24,3 | 65,9 | 5,2 | 24,3 |
| III | 201 | $C_{19}H_{18}N_6O$ | 66,2 | 5,3 | — | 65,9 | 5,2 | — |
| IV | 189—190 | $C_{18}H_{15}N_7O_3$ | 57,0 | 4,0 | — | 57,3 | 4,0 | — |
| V | 160 | $C_{18}H_{15}N_7O_3$ | 57,5 | 4,4 | 25,8 | 57,3 | 4,0 | 26,0 |
| VI | 130—131 | $C_{19}H_{18}N_6O \cdot {}^1/_2C_5H_5N$ | 66,8 | 5,4 | 24,5 | 66,9 | 5,3 | 24,7 |
| VII | 131 | $C_{18}H_{16}N_6$ | 68,5 | 5,2 | 26,6 | 68,3 | 5,1 | 26,6 |
| VIII | 130 | $C_{19}H_{17}N_7O_3$ | 58,4 | 4,6 | 24,5 | 58,3 | 4,4 | 25,0 |

they exist in tautomeric forms D, E, and F. However, form D can be excluded for formazans I-V, inasmuch as they contain two nonequivalent N−H bonds that cannot give only the single $\nu_{NH}$ absorption band that we observed. Consequently, the most probable forms in which the existence of these compounds is possible are E and F, and the band at 3384-3390 cm$^{-1}$ is related to the stretching vibrations of the N−H group.

Formazans VI-VIII, which contain H and OCH$_3$ substituents in the 4 position of the pyrimidine ring, have $\nu_{N-H}$ 3334-3360 cm$^{-1}$ and may exist in tautomeric forms A and B (form A is the most likely form according to the pK$_a$ values).

The acid−base properties of the synthesized compounds were studied. The ionization constants were determined by spectrophotometry inasmuch as, for formazans I-VII, conversion to the anion is accompanied by a large bathochromic effect. As seen from the data in Table 1, the ionization constants of formazans I-III range from 8.5 to 8.9, whereas the ionization constants of VI and VII range from 13.1 to 13.3. 1-(6'-Methyl-4'-hydroxy-2'-pyrimidyl)-3-phenyl-5-[p(o)-nitrophenyl]formazans IV and V have two ionization constants: The first is close to the ionization constants of formazans I-III, while the second is close to the ionization constants of VI and VII, i.e., a dianion is formed in the dissociation of nitrophenyl-containing formazans IV and V. On the basis of data from a study of the acid properties of pyrimidine derivatives (the pK$_a$ value of 4-pyrimidone is 8.6 [2]) and benzazolylformazans [4-6], we arrived at the conclusion that the initial dissociation proceeds at the N−H bond of the pyrimidine ring. The detachment of the second hydrogen leads to a formazan anion. The absence of a second ionization constant in the case of formazans I-III can be explained by the fact that the resulting anion increases the electron density of the formazan chain while reducing the acid properties of the N−H group, and the $pK_a$ values lie beyond the limits of our measurements. The introduction of a strong acceptor such as a nitro group decreases the electron density of the formazan grouping, the acidity of the N−H group increases, and it becomes possible to determine the second ionization constant. The measurement of the ionization constant of 1-(6'-methyl-4'-methoxy-2'-pyrimidyl)-3-phenyl-5-(p-nitrophenyl)formazan (VIII) confirms this assumption: Its $pK_a$ value is one unit lower than the $pK_a$ value of VI (Table 1).



X = H, $OCH_3$; R = H, p(o)-$CH_3$, p(o)-$NO_2$

Formazans containing a pyrimidine ring seemed of interest with respect to the search for new tetrazolium salts − potential histochemical reagents and biological indicators. In this connection, we investigated the reaction of the compounds under consideration with N-bromosuccinimide (NBS) which leads to tetrazolium salt [7]. However, we did not isolate tetrazolium salts of 1-(2'-pyrimidyl)-3,5-diphenylformazans. Like the tetrazolium salts of 1-benzoxazolyl-5-phenyl-formazans [8], they proved to be unstable and decomposed at the moment of formation to 2,5-disubstituted tetrazoles.

## EXPERIMENTAL

The IR spectra of saturated solutions of the formazans in $CCl_4$ were recorded with a UR-20 spectrometer (at 3100-3500 $cm^{-1}$ with a LiF prism). The electronic spectra were recorded with an SF-18 spectrophotometer. The ionization constants ($pK_a$) were determined spectrophotometrically as in [9]. The optical density of 50% alcohol buffer solutions (acetate−ammonia buffer) were determined at the wavelength corresponding to $\lambda_{max}$ of the sodium salts of the formazans (C-formazans $1 \cdot 10^{-5}$ g-mole/liter). The ionization constants of VI-VIII and the second ionization constants of IV and V were calculated by the graphical method [9] used for acids whose $pK_a$ values are higher than 11.

1-(6'-Methyl-4'-hydroxy-2'-pyrimidyl)-3,5-diphenylformazan (I). A solution of a diazonium compound obtained from 0.4 g (0.05 mole) of aniline was added to a cooled solution of 0.9 g (0.04 mole) of benzaldehyde 6-methyl-4-hydroxy-2-pyrimidylhydrazone in 80 ml of alcoholic alkali (4 : 1), after which the mixture was neutralized to pH ~ 7 with 2N HCl, and the resulting precipitate was removed by filtration and washed with a small amount of water to give a product with mp 188-189° (alcohol).

Formazans II-VIII were similarly obtained, and their melting points and results of elementary analysis are presented in Table 2. The yields ranged from 50 to 70%.

2,5-Diphenyltetrazole. A warm solution of 1.5 g (0.08 mole) of NBS in 20 ml of glacial acetic acid was added to a solution of 0.7 g (0.03 mole) of 1-(6'-methyl-4'-hydroxy-2'-pyrimidyl)-3,5-diphenylformazan in 20 ml of DMF, after which the mixture was refluxed for 15 min until the light-brown color of the solution no longer vanished. The solution was then cooled and neutralized to pH ~ 7 with 2 N NaOH. The mixture was worked up to give 2,5-diphenyltetrazole with mp 99° (alcohol) and $\lambda_{max}$ 270 nm (literature mp 101° [10]; $\lambda_{max}$ 270 nm [11]). No melting-point depression was observed for a mixture of this product with an authentic sample. The same compound was also isolated in the case of the reaction of formazan VI with NBS.

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