The k1 and k2 rate constants were calculated from the equations

 $k_1 = [\ln h_m / (h_m - h_t)] \cdot 1/t; \ k_2 = k_1 / [\text{HCl}]^n,$ 

where  $k_1$  is the first-order rate constant (in reciprocal seconds),  $h_m$  is the height of the wave of the reduction of the aldehyde (in millimeters) corresponding to the total hydrolysis,  $h_t$  is the height of the reduction wave at time t (in millimeters), and  $k_2$  is the second-order rate constant (in liters/mole-sec). The error in the determination by the polarographic method was 2-8%.

 $1-[\alpha-(\text{Ethoxy})\text{ethyl}]$ benzimidazole-2-thione (VII). A solution of 1.76 g (0.01 mole) of thione I in 10 ml of ethanol was added dropwise to 10 ml of absolute ethanol saturated with dry HCl, and the mixture was refluxed for 2 h. It was then cooled and worked up to give 1.42 g (64%) of VII with mp 92-93°C. Found: C 59.4; H 6.4; S 14.5%. C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>OS. Calculated: C 59.4; H 6.3; S 14.4%.

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STRUCTURE OF 3-CHLORO-6-HYDRAZINOPYRIDAZINE IN SOLUTIONS

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It is shown by means of the fixed-structure method, UV spectroscopy and dipolemoment method that the product of the reaction of 3,6-dichloropyridazine with hydrazine in solution in methanol and acetonitrile has the 3-chloro-6-hydrazinopyridazine structure.

The 3-chloro-6-pyridazinone hydrazone structure (XI, R = H, and  $R' = NNH_2$ ) was assigned to the product of the reaction of 3,6-dichloropyridazine (II) with hydrazine (compound A), since the UV spectrum of a solution of  $CH_3OH$ , like the spectrum of 3-hydroxy-6-pyridazinone, contains an absorption band at 324 nm ( $\epsilon$  1270) [1].



A more detailed analysis of the UV spectra recorded in hexane, methanol, dioxane, and acetonitrile of pyridazine I and its derivatives II-VII, which are incapable of tautomeric transformations showed that an absorption band with  $\lambda_{max} \ge 310$  nm appears in the spectra of most of them, often in the form of a shoulder (Table 1). The spectra of I-VII in hexane,

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TABLE 1. UV Spectra and Dipole Moments of Pyridazine (I-X) and Pyridazone (XII-XV) Derivatives

10			80	$\lambda_{\max}$ , nm (log $\epsilon$ )		
Com	R	R'	mp, °C	CH3OH	CH₃CN	ца, D
I	Н	н	_	238 (2,95) <sup>b</sup> , 243 (3,06), 253 (2,85) <sup>b</sup> , 312 (2,38)	$238 (2,79)^{b}, 243 (2,93), 253 (2,72) 324 (2,32)$	4,09
Π	C1	CI	65—67	216 (3,91), 272 (3,06), 307 (2,53)	216(3,92), 272(3,07), 310(2,60)	4,44
Ш	C1	OCH₃	9191,5	217 (3,87), 281 (3,28), 314 (2,47)b	$217 (3,84), 280 (3,24), 312 (258)^{b}$	3,55
IV V	OCH₃ OPh	OCH₃ OPh	$105 - 106 \\ 140 - 141$	213 (3,84)b, 287 (3,32) 222 (4,25), 287 (3,30), 317 (2,73)b	$212 (3,87)^{b}, 289 (3,31)$ 220 (4,28), 288 (3,30), $322 (2,60)^{b}$	
ΥI	Cl	N(CH₃)₂	100—101	222 (3,94), 257 (4,20), 345 (3,15)	220(3,91), 257(4,22), 324(3,11), 342(3,18)	5,62
VII	Cl	N(CH₃)NH₂	108—109	218 (3,97), 257 (4,18), 338 (3.14)	216 (3,90), 254 (4,16), 331 (3,11)	5,49
VIII	CI	NHNH <sub>2</sub>	138—139	213 (3,96), 247 (4,06), 324 (3,14)	207 (3,92), 247 (4,08), 320 (3,18)	5,06
IX	Cl	$N(CH_3)N =$	130—131	$225 (4,12), 242 (4,03)^{b},$	232 (4,08), 321 (4,53)	
Х	CI	NHN=CHPh	257—258	$226 (4,08), 242 (4,00)^{b},$	229 (4,03), 238 (4,02) <sup>b</sup> , 216 (4,51)	
XII XIII XIV	H CH₃ CH₃	O O NNH2	140—141 89 90—92	$\begin{array}{c} 317 & (4,02) \\ 228 & (3,74) b, 302 & (3,29) \\ 231 & (3,60), 305 & (3,39), \\ 228 & (4,01), 240 & (3,97) b, \\ 271 & (2,02) & (4,02) \\ 371 & (2,02) & (4,02) \\ 371 & (4,02) & (4,02) & (4,02) \\ 371 & (4,02) & (4,02) & (4,02) \\ 371 & (4,02) & (4,02) & (4,02) \\ 371 & (4,02) & (4,02) & (4,02) \\ 371 & (4,02) & (4,02) & (4,02) & (4,02) \\ 371 & (4,02) & (4,02) & (4,02) & (4,02) \\ 371 & (4,02) & (4,02) & (4,02) & (4,02) & (4,02) & (4,02) \\ 371 & (4,02) &$	228 (3,60), 302 (3,29) 232 (3,61), 310 (3,42), 228 (4,00), 242 (3,98) <sup>b</sup> , 275 (2, 27) 428 (9,27)	1,78 1,79 2,33
XV	CH₃	NN=CHPh	108110	231 (4,19),336 (4,44), 410 (3,36) <sup>b</sup>	232 (4,18), 340 (4,48), 412 (3,35) b	-

<sup>a</sup>In dioxane at 25°C. <sup>b</sup>Shoulder.

dioxane, and acetonitrile do not differ substantially. On passing from chloro and meth(phen)oxy derivatives II-V to amino and hydrazino derivatives VI and VII one observes a hypsochromic shift of the average absorption band ( $\Delta\lambda \approx 30$  nm) and a change in the ratio of the intensities of the short-wave and average bands (Table 1). The intensity of the long-wave band also increases in the spectra of 3-chloro-6-dimethylaminopyridazine (VI) and 3-chloro-6-(1-methyl-1-hydrazino)pyridazine (VII). An analysis of the UV spectra of compound A and of models with fixed structures, viz., hydrazine VII and 3-chloro-6-pyridazinone hydrazone (XIV) (Fig. 1), as well as an examination of the effect of the substituent in pyridazine derivatives (Table 1), makes it possible to conclude that compound A has the 3-chloro-6-hydrazinopyridazine structure (VIII) rather than hydrazone structure XI in solutions inmethanol and acetonitrile. This conclusion is also confirmed by data from the dipole-moment method. Like phthalazine derivatives [2], pyridazine and its derivatives, including hydrazine VIII, have higher dipole moments than pyridazinones XII and XIII or hydrazone XIV (Table 1).

The difference in the chemical shifts of the 4-H and 5-H protons and their spin-spin coupling constants  $(J_{\rm HH}^3)$  in the PMR spectra of the compounds with pyridazine (I-X) and pyridazinone (XII-XV) structures is small and cannot serve as a diagnostic sign for the identification of the tautomeric forms (Table 2).

According to the UV spectroscopic data, hydrazine VIII does not undergo any changes in  $CH_3OH$  and  $CH_3CN$  for a considerable time (no less than 5 days). However, when a solution of it in dioxane is allowed to stand for more days, it undergoes transformations, as a result of which the intensity of the band at 247 nm ( $\Delta \epsilon \approx 100$ ) decreases somewhat, and a shoulder ap-



- Fig. 1. UV spectra of hydrazines VII (1) and VIII (2) and hydrazone XIV
- (3) in methanol.

TABLE 2. PMR Spectra of Pyridazines II-IV and VI-VIII, Pyridazzones XII and XIII, and Hydrazone XIV

Com-	Columnt		1 4H-5H			
pound	Solvent	4-H	5-H	other protons	Hz	
II II IV VI VII VII VIII VIII XIII XIII	CCl <sub>4</sub> DMSO CCl <sub>4</sub> CCl <sub>4</sub> DMSO Dioxane DMSO Dioxane DMSO Dioxane DMSO Dfoxane CCl <sub>4</sub>	7,6 8,0 7,39 d 6,5 7,46 d 7,52 d 7,52 d 7,52 d 7,52 d 7,52 d 7,52 d 7,52 d 7,52 d 7,34 d 7,54 d 7,54 d 7,54 d 7,16 d 7,08 d 7,25 d	4 \$ 6,95 d 2 \$ 7,17d 7,20d 7,06d 7,06d 7,06d 7,06d 6,94d 6,87d 6,68d 6,50d 6,51 d	$\begin{array}{c} &$	$\begin{array}{c}$	

<sup>a</sup>Broad signal. <sup>b</sup>The  $\delta NH_2$  value in CHCl<sub>3</sub> is 4.07 ppm, as compared with 4.20 ppm in PhCN. <sup>C</sup>Merging of the signals due to exchange processes. <sup>d</sup>The  $\delta NH_2$  value in CHCl<sub>3</sub> is 4.0 ppm, as compared with 4.16 ppm in PhCN.

pear at 270 nm. Hydrazine VIII is virtually insoluble in hexane. However, if a mixture of it and hexane is allowed to stand for 2-3 days or is heated, a relatively intense band at 268 nm and a low-intensity band at 317 nm appear in the spectra. Hydrazine VIII evidently undergoes isomerization to 3-chloro-6-pyridazinone hydrazone (XI) in this case, whereas a tautomeric equilibrium of two forms exists in dioxane. This assumption requires more rigorous proof. However, in the phthalazine series, as demonstrated in [3], the hydrazone form proved to be the most stable form. The difference in the stabilities of the tautomeric hydrazino-substituted derivatives of pyridazine and phthalazine can evidently be explained by the effect of annelation. Thus the product of diazo coupling of the benzenediazonium salt with phenol exists in the crystalline state and in solutions primarily in the azo form. The product of coupling with naphthol can be separated into azo and hydrazone forms, which exist in tautomeric equilibrium in solutions, whereas the product of coupling with 9-anthrol exists only in the hydrazone form (see the literature cited in [4]).

The product of condensation of hydrazine VIII with benzaldehyde can also exist in two tautomeric forms, viz., hydrazone X and mixed azine XVI (R=H, R'=NN=CHPh). A comparison of its UV spectra with the spectra of benzaldehyde N-methyl-N-(3-chloro-6-pyridazinyl)hydra-zone (IX) and l-methyl-3-chloro-6-pyridazinone benzylidenehydrazone (XV) makes it possible to prefer benzaldehyde (3-chloro-6-pyridazinyl)hydrazone structure (X); its spectra in hexane, dioxane, CH<sub>3</sub>CN, and CH<sub>3</sub>OH are virtually identical. No changes whatsoever are observed during storage of solutions of hydrazone X.

Hydrazine VII was synthesized from 3,6-dichloropyridazine II and methylhydrazine. Upon reaction with benzaldehyde it gave hydrazone IX, whereas 3-chloro-6-methylaminopyridazine, which was identical to the product obtained from II and methylamine by the method in [5], was isolated in the case of deamination with HNO<sub>2</sub>.

## EXPERIMENTAL

See [2] for the conditions used for the physicochemical measurements. Pyridazine was obtained by hydrogenation of II by means of the method in [6], II-VI, VIII, XII, and XIII were obtained by the methods in [1, 5-7], and hydrazone X was obtained by the method in [8].

<u>3-Chloro-6-(1-methyl-1-hydrazino)pyridazine (VII).</u> A 2.5-ml (42 mmole) sample of methylhydrazine was added to a hot solution of 2 g (13 mmole) of 3,6-dichloropyridazine (II) in 5 ml of ethanol, and the mixture was heated to the boiling point and allowed to stand at 20-25°C until a precipitate formed; the latter was removed by filtration, washed with water, and recrystallized from water to give 1.1 g (52%) of shiny white needles with mp 108-109°C. IR spectrum (mineral oil): 3290, 3195 cm<sup>-1</sup> (NH<sub>2</sub>). UV spectrum  $\lambda_{max}$  (log  $\varepsilon$ ): in hexane 213 (3.89), 251 (4-21), and 322 nm (3.20); in dioxane 218 (3.88), 256 (4.18), and 330 nm (3.17). Found: C 38.4; H 4.6; Cl 22.4; N 35.3%. C<sub>5</sub>H<sub>7</sub>ClN<sub>4</sub>. Calculated: C 37.9; H 4.5; Cl 22.4; N 35.3%.

Benzaldehyde N-Methyl-N-(3-chloro-6-pyridazinyl)hydrazone (IX). A drop of AcOH and 0.65 ml (5.5 mmole) of benzaldehyde were added to a solution of 0.4 g (2.5 mmole) of hydrazine VII in 7 ml of ethanol, and the solution was refluxed for 30 min. It was then cooled, and the precipitate was removed by filtration, washed with water, dried, and recrystallized from petroleum ether (bp 70-100°C) to give 0.6 g (97%) of white crystals of hydrazone IX with mp 130-131°C. UV spectrum,  $\lambda_{max}$  (log  $\varepsilon$ ): in hexane 228 (4.12) shoulder, 236 (4.14), and 322 (4.55); in dioxane 237 (4.15) and 325 nm (4.53). Found: 58.3; H 4.5; Cl 14.3; N 22.8%. C12H11ClN4. Calculated: C 58.4; H 4.5; Cl 14.4; N 22.7%.

1-Methyl-3-chloropyridazinone Hydrazone and Azine (XIV) and XXVII). A 2.1-ml sample of dimethyl sulfate was added to a solution of 2.3 g (15.4 mmole) of 3,6-dichloropyridazine in 10 ml of dry chlorobenzene, and the mixture was heated carefully until it began to boil. After the solution separated into layers, it was cooled, and the resulting white hygroscopic precipitate of 1-methyl-3,6-dichloropyridazinium methylsulfate was removed rapidly by filtration and washed with five 5-ml portions of cold dry benzene. The resulting salt was dissolved in 30 ml of absolute  $CH_3OH$ , and the solution was added dropwise to a solution of 1.4 g (44 mmole) of anhydrous hydrazine in 10 ml of absolute CH3OH with vigorous stirring at 0°. The precipitate was removed by filtration, washed with absolute CH<sub>3</sub>OH, and recrystallized from ethanol to give 0.2 g (10%) of azine XVII in the form of shiny claret-colored needles with mp 254°C. UV spectrum,  $\lambda_{max}$  (log  $\varepsilon$ ): in CH<sub>3</sub>CN 322 (4.50), 333 (4.49), and 470 nm (3.40); in dioxane 323 (4.47), 335 (4.46), and 468 nm (3.38). Found: C 42.3; H 3.6; Cl 24.9; N 29.4%. C10H10Cl2N6. Calculated: C 42.1; H 3.5; Cl 24.9; N 29.5%.

The filtrate and wash CH3OH were combined, the methanol was removed without heating, and the residue was treated with ether. The precipitate that formed after evaporation of the ether was recrystallized from hexane (cooled to -10 °C) to give 0.6 g (25%) of colorless crystals of hydrazone XIV with mp 90-92°C. UV spectrum,  $\lambda_{max}$  (log  $\epsilon$ ): in hexane 225 (4.05), 243 (3.88) shoulder, 268 (3.78), and 415 nm (2.84); in dioxane 225 (3.97), 242 (3.92), shoulder, 278 (3.85), and 432 nm (2.84). Found: C 38.0; H 4.4; Cl 22.3; N 35.2%. C5H7ClN4. Calculated: C 37.9 H 4.4; Cl 22.3; N 35.3%.

1-Methyl-3-chloropyridazinone Benzylidenehydrazone (XV). One drop of AcOH and 0.16 ml (1.5 mmole) of benzaldehyde was added to a solution of 0.2 g (1.3 mmole) of hydrazone XIV in 5 ml of C<sub>2</sub>H<sub>5</sub>OH, and the mixture was refluxed for 2 h. It was then cooled, and the precipitate was removed by filtration, washed with alcohol, and recrystallized from alcohol to give 0.2 g (64%) of azine XV with mp 108-110°C in the form of a brick-red powder. UV spectrum,  $\lambda_{max}$  (log  $\epsilon$ ): in hexane 232 (4.20), 327 (4.45), 340 (4.49), and 419 nm (3.28); in dioxane 231 (41.9), 336 (4.45), and 410 nm (3.36). Found: C 58.3; H 4.5; N 22.8%. C12H11CIN4. Calculated: C 58.4; H 4.5; N 22.7%.

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