SYNTHESIS OF SOME AZO COMPOUNDS AND A STUDY OF THEIR PROPERTIES

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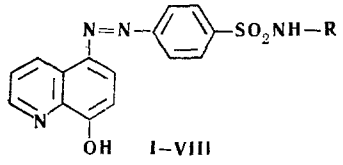
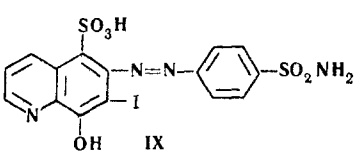
11 azo compounds hitherto undescribed in the literature are synthesized. The azo components used were 8-hydroxyquinoline, resorcinol, pyrogallol, and 7-iodo-8-hydroxy-5-quinolinesulfonic acid, while the diazol components were sulfanilamide and a number of its derivatives. The acid dissociation constants for 8 azo compounds are determined by a solubility method and also spectrophotometrically. The constants are of the order 10^{-7}–10^{-9}.

In order to study the properties of complex compounds formed by orthohydroxyazo compounds and some transition metals, we have synthesized 11 azo compounds hitherto undescribed in the literature. The azo components were 8-hydroxyquinoline, resorcinol, pyrogallol, and 7-iodo-8-hydroxy-5-quinolinesulfonic acid, and the diazo components were sulfanilamide and a number of its derivatives.

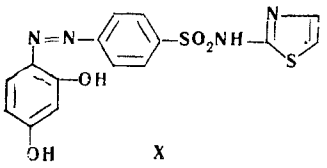
The following are the formulas of the compounds prepared:



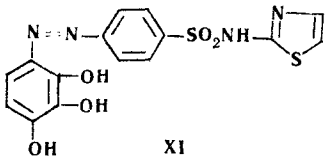
I–VIII



IX

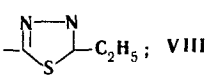
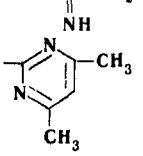


X



XI

I R = H; II R = $COCH_3$; III R = CN; IV R = $CONH_2$; V R = $C(=NH)-NH_2$;

VI R =  ; VII R =  ; VIII R = 

I) 5-(p-sulfamidobenzenazo)-8-hydroxyquinoline; II) (p-cyanosulfamidobenzenazo)-8-hydroxyquinoline, IV) 5-(p-ureidosulfonylbenzenazo)-8-hydroxyquinoline, V) 5-(p-guanidinosulfonylbenzenazo)-8-hydroxyquinoline, VI) 5-[p-(thiazolyl-2)sulfamidobenzenazo]-8-hydroxyquinoline, VII) 4-[p-(5-ethyl-3,4-thiodiazolyl-2)sulfamidobenzenazo]-8-hydroxyquinoline, VIII) 5-[p-(4,6-dimethylpyrimidyl-2)sulfamidobenzenazo]-8-hydroxyquinoline, IX) 5-sulfo-6-(p-sulfamidobenzenazo)-7-iodo-8-hydroxyquinoline, X) 4-p-(thiazolyl-2)sulfamidobenzenazo resorcinol, XI) 4-[p-(thiazolyl-2)sulfamidobenzenazo]pyrogallol.

The spectroscopic properties of compounds I–VIII are shown in Fig. 1.

The compounds studied being weak acids, their acid dissociation constants were determined by the solubility method [1–3]. The dissociation constants were also determined spectroscopically [4, 5] (Table 2).

EXPERIMENTAL

5-(p-Acetylsulfamidobenzenazo)-8-hydroxyquinoline. To 40.0 g (0.17 mole) sodium-sulfacyl in 75.0 g (0.8 mole) concentrated HCl plus 100 ml water was added a solution of 10.4 g (0.15 mole) $NaNO_2$ in water. Diazotization took 20 min, and the temperature was 0–10°. A solution of 15.0 g (0.4 mole) NaOH and 17.12 g (0.12 mole) 8-hydroxyquinoline in water was cooled to 5–10°, and added in small portions to the diazonium chloride solution. The mixture was left for 1 hr. The progress of the azo coupling was followed by taking a "discharge" sample. The reactants were kept alkaline (pH 9–10). The azo compound prepared was precipitated by acidifying with HCl, and purification was by recrystallizing from water and EtOH [6, 7]. The other compounds were synthesized similarly.

Determining the acid dissociation constant by the solubility method. The azo compounds were shaken at room temperature, until saturation was obtained, with water and solutions of NaOH of the following concentrations: $1.0 \cdot 10^{-3}$ M; $2.5 \cdot 10^{-3}$ M; $5.0 \cdot 10^{-3}$ M; $5.0 \cdot 10^{-2}$ M. The amount of the substance in the filtrate (after centrifuging and filtering through a close filter) was determined. The method of determination was a bromometric one [8]. Initially it was established that it was possible to make such a determination, and the number of equivalents of $KBrO_3$ used

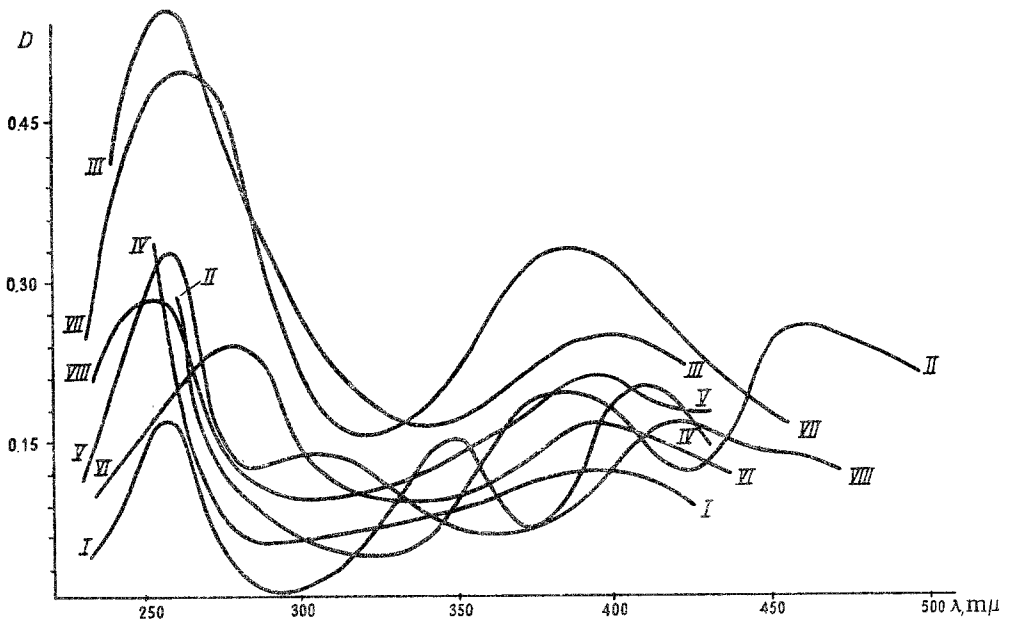


Fig. 1. Spectroscopic properties of azo compounds (numbering corresponds to the numbering of the compounds in the text).

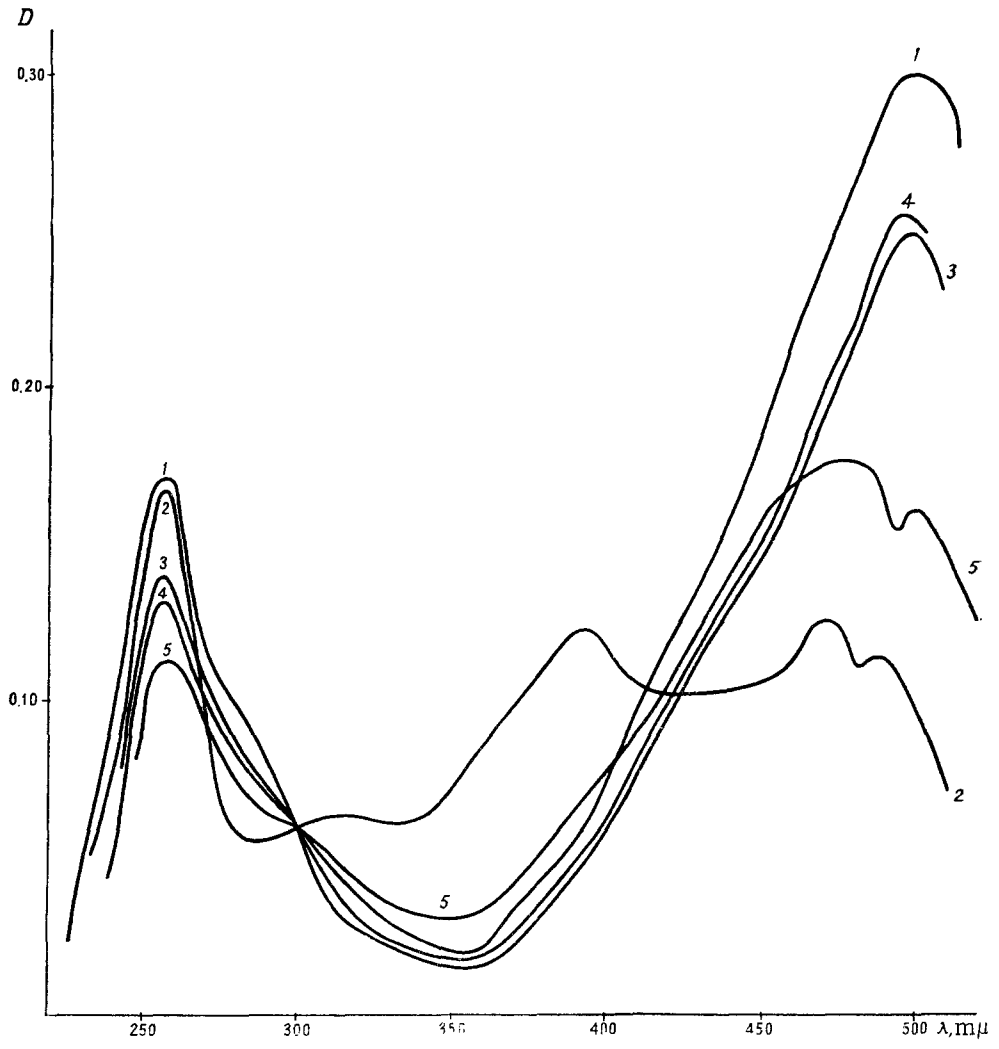


Fig. 2. Optical density plots for 5-(p-sulfamidobenzenazo)-8-hydroxyquinoline (I) (for $1.7 \cdot 10^{-5}$ M). I—pH 11.70; 2—pH 3.10; 3—pH 10.15; 4—pH 9.55; 5—pH 8.35.

Table 1

Properties of the Azo Compounds

Compound no.	Color	Mp, °C	Solubility*									Formula	N, %		Yield, %
			w	Et	Me	e	Ac	Py	Bz	C	Cl		Found	Calculated	
I	Cherry red	239—241 (decomp)	±	++	++	+	+	++	±	±	+	$C_{15}H_{12}N_4O_3S$	16.73	17.07	85.1
II	Orange	221—222	±	++	++	—	+	++	—	—	—	$C_{17}H_{14}N_4O_4S$	14.91	15.13	85.0
III	Red	154	+	++	++	+	++		—	—	+	$C_{16}H_{11}N_5O_3S$	19.39	19.83	88.3
IV	Cherry red	145	+	++	++	—	+	±	—	—	—	$C_{16}H_{13}N_5O_4S$	18.61	18.86	74.7
V	Dark cherry	204—207	±	+	+	—	+	++	—	—	—	$C_{16}H_{14}N_6O_3S$	22.24	22.7	84.4
VI	Brick red	232—233 (decomp)	+	++	++	—	++	++	—	—	+	$C_{18}H_{13}N_5O_3S_2$	16.65	17.03	92.0
VII	Orange yellow	235—237	+	++	+	+	+	++	+	—	+	$C_{19}H_{16}N_6O_3S_2$	18.56	19.09	81.8
VIII	Pale red	143	±	++	++	±	++	++	++	+	+	$C_{21}H_{17}N_6O_3S$	19.23	19.38	75.6
IX	Reddish brown	136	++	+	++		+	++				$C_{15}H_{11}IN_4O_6S_2$	10.15	10.45	65.6
X	Orange	197	+	++	++	+	++	++	—	+	+	$C_{15}H_{12}N_4O_4S_2$	14.48	14.89	88.3
XI	Dark brown	122 (decomp)	+	++	++	+	++		+	—	—	$C_{15}H_{12}N_4O_5S_2$	14.17	14.28	64.6

*w—water, Et—EtOH, Me—MeOH, e—ether, Ac—acetone, Py—pyridine, Bz—benzene, C—CCl_4, Cl—$CHCl_3$; ++ good solubility; + soluble, —insoluble.

up per 1 mole of the substance under investigation, was determined. For example in brominating I 3.657 equivalents of $KBrO_3$ used, II—3.648; III—2.046; IV—5.061; V—3.204; VI—5.258; VII—1.010; IX—6.800; X—6.294. The hydrogen ion concentration was determined with a P-4 potentiometer and a quinhydrone electrode, and in part of the experiments with a LP-58 laboratory pH meter with a glass electrode.

Table 2

Acid Dissociation Constants of the Azo Compounds

Compound	Dissociation constants	
	Solubility method	Spectrophotometric method
I	$0.3 \cdot 10^{-9}$	$0.3 \cdot 10^{-9}$
II	$0.7 \cdot 10^{-9}$	$0.4 \cdot 10^{-9}$
III	$1.4 \cdot 10^{-8}$	$0.4 \cdot 10^{-8}$
IV	$0.4 \cdot 10^{-8}$	$0.2 \cdot 10^{-8}$
V	$0.7 \cdot 10^{-8}$	$0.4 \cdot 10^{-8}$
VI	$0.8 \cdot 10^{-7}$	$0.7 \cdot 10^{-7}$
VII	$0.4 \cdot 10^{-7}$	$0.2 \cdot 10^{-7}$
VIII	$0.9 \cdot 10^{-7}$	$0.7 \cdot 10^{-7}$

In addition the acid dissociation constants were determined spectroscopically, by the method of isobestic points. As this method uses the difference in absorption spectra between the acid and its dissociated form, solutions of different pH of the compound under investigation were prepared. Reagents were 0.1 N solutions of $HClO_4$, $NaClO_4$, and NaOH. They had constant ionic strength, 0.1. For example, to determine the constant of I, 5 solutions were made up, with pH 3.10, 8.35, 9.55, 10.15 and 11.70. The solution containing the undissociated form (pH 3.10) was prepared as follows. Into a 100 ml measuring flask was put 10 ml $1.7 \cdot 10^{-5}$ M solution of I, then 1 ml $HClO_4$, 10 ml $KClO_4$, and the mixture made up to 100 ml with water. To prepare a solution containing the dissociated form of I (pH 11.70), 10 ml solution of I was put into a measuring flask of the same capacity, and that was followed by 10 ml NaOH solution. To make solutions containing mixtures of dissociated and undissociated forms of I, 10 ml solution of I was taken, and varying amounts of NaOH and $NaClO_4$ solution added. Fig. 2 shows the light absorption curves of these solutions. The results of determinations by the two methods are given in Table 2. Table 2 shows that the value of the constant increases somewhat when the amide group is replaced by an acetamido one, urea, guanidine, cyanamide, ethylthiodiazol, dimethylpyrimidine, and thiazole.

We first used the solubility method to determine dissociation constants of azo compounds.

Spectrophotometric determinations were carried out with an SF-4 spectrophotometer.

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