SYNTHESIS AND STUDY OF THE PROPERTIES OF SOME AZOMETHINE COMPOUNDS

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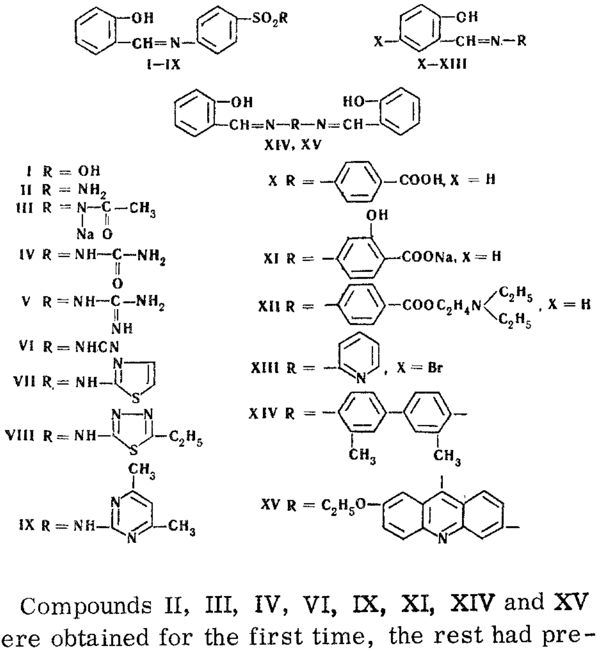
8 azomethine compounds hitherto undescribed in the literature, which are derivatives of salicylaldehyde and amines from the group sulfanilamide, acridine, tolidine, and some other compounds, are synthesized. The acid dissociation constants of the azomethines are determined spectrophotometrically (using the isobestic points method), and by the solubility method. These constants are of the order 10^{-7}–10^{-11}.

Azomethine compounds prepared from aromatic o-hydroxyaldehydes or o-hydroxyketones and primary amines, can give stable complexes with various cations [1, 2]. The present paper consider the properties of azomethine compounds of the group sulfanilamides, acridine, tolidine, and certain other compounds. These azomethines are derivatives of salicylaldehyde: salicylalsulfanilic acid (I), p-salicylalsulfanilamide (II), N-(p-salicylalsulfanil)sodioacetamide (III), p-salicylalsulfanilurea (IV), p-salicylalsulfanilguanidine (V), p-salicylalsulfanilcyanamide (VI), 2-(p-salicyalsulfanilamino)thiazole (VII), 2-(p-salicylalsulfanilamino)-5-ethyl-3,4-thiodiazole (VIII), 2-(p-salicylalfanilamido)-4,6-dimethylpyrimidine (IX), salicylalanthranilic acid (X), sodium 4-salicylalaminosalicylate (XI), diethylaminoethyl p-salicylalaminobenzoate (XII), 2-(5-bromo-2-hydroxybenzylamino)pyridine (XIII), N, N'-disalicylal-o-tolidine (XIV), and 3,9-disalicylalamino-7-ethoxyacridine (XV).



Compounds II, III, IV, VI, IX, XI, XIV and XV were obtained for the first time, the rest had previously been synthesized [3, 4]. The azomethines obtained are stable to acid and alkali. Their alkaline solutions are yellow, and the acid ones decolorize, addition of alkali restoring the yellow color. Compounds III and XI are sodium salts of azomethines. Fig. 1 gives the spectroscopic characteristics of II, III, and V.

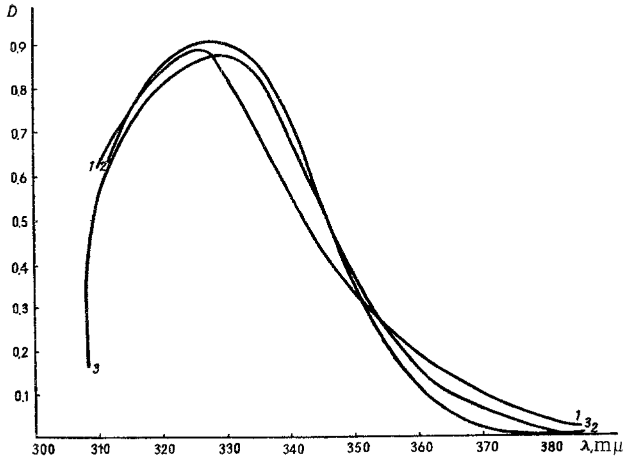


Fig. 1. UV spectra: 1) V (with $6.2 \cdot 10^{-4}$ M, pH 2.50); 2) III (with $5.9 \cdot 10^{-4}$ M, pH 2.60); 3) II (with $7.2 \cdot 10^{-4}$ M, pH 3.01).

The azomethines investigated behave as weak acids. To determine their acid dissociation constants, we firstly used the method based on determining solubilities in water at various pHs. This method was previously used to determine the dissociation constants of dimethylglyoxime, [5], 5,7-dibromohydroxyquinoline [6], and a number of Mannich bases [7].

For azomethines II-VIII the dissociation constants were determined spectrophotometrically as well, by the method of isobestic points, in which use is made of the change in light absorption of an acid solution for different pHs [8, 9].

EXPERIMENTAL

Synthesis of the azomethines was effected by directly condensing the appropriate amine with salicylaldehyde [10]. Stoichiometric amounts of these substances, dissolved in EtOH or MeOH, were refluxed for 30–60 min in a flask. The amines and salicylaldehyde were used in the ratios 1:1 or 1:2 (in the cases of Rivanol and o-tolidine). After cooling the crystals which separated were filtered off. The compounds obtained were purified by recrystallizing from MeOH, EtOH, or dioxane.

Figure 2 gives a photomicrograph of crystals of p-salicylalsulfanilamide.

Table 1

Azomethines, Derivatives of Salicylaldehyde

Compound	Color	Mp, °C	Solubility	Formula	N, %		Yield, %
					Found	Calculated	
II	Yellow	208—209	Readily soluble in hot EtOH and MeOH, iso-AmOH, n-BuOH, acetone and water $2 \cdot 10^{-3}$ mole/l.	$C_{13}H_{12}N_2O_3S$*	11.13 11.18	10.14	60
III	Yellow	228—230 (decomp)	Readily soluble in water and MeOH, less soluble in EtOH, almost insoluble in ether and n-BuOH, insoluble in benzene and acetone.	$C_{15}H_{13}NaN_2O_4S$**	7.92 7.70	8.23	58
IV	Yellow	196	Soluble in EtOH and MeOH, and in benzene.	$C_{14}H_{13}N_3O_4S$	13.21	13.16	93
VI	Yellow	236—239	Readily soluble in acetone, pyridine, slightly soluble in water, alcohols (EtOH, iso-AmOH, n-BuOH).	$C_{14}H_{11}N_3O_3S$	13.34	13.94	57
IX	Yellow	167—170	Slightly soluble in EtOH and MeOH.	$C_{19}H_{18}N_4O_3S$	14.04	14.65	73
XI	Yellow	235 (decomp)	Soluble in water, EtOH, MeOH, less soluble in acetone, insoluble in benzene.	$C_{14}H_{10}NaNO_4$	5.49	5.01	90
XIV	Orange	199—200	Soluble in dioxane and formamide, in water $3 \cdot 10^{-5}$ mole/l. Insoluble in EtOH and MeOH.	$C_{28}H_{24}N_2O_2$***	6.41 6.41	6.66	68
XV	Orange	230	Readily soluble in EtOH, MeOH, iso-AmOH, n-BuOH, and in pyridine and water.	$C_{29}H_{27}N_3O_3$	9.54 9.64	9.10	83

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*Found: C56.50; 56.56; H 4.10; 4.13%. Calculated C 56.49; H 4.38%.

**Found: C 48.97; 48.73; H 4.32; 4.23%. Calculated C 52.95; H 3.85%.

***Found: C 79.23; 73.20; H 5.88; 5.96%. Calculated C 79.97; H 5.75%.

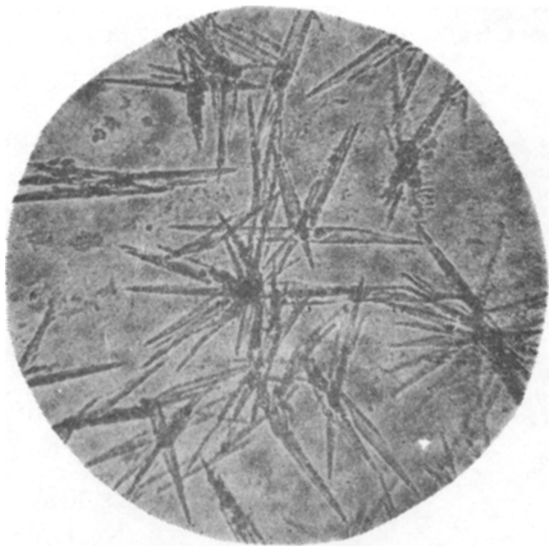

Fig. 2. Crystals of p-salicylalsulfanilamide.

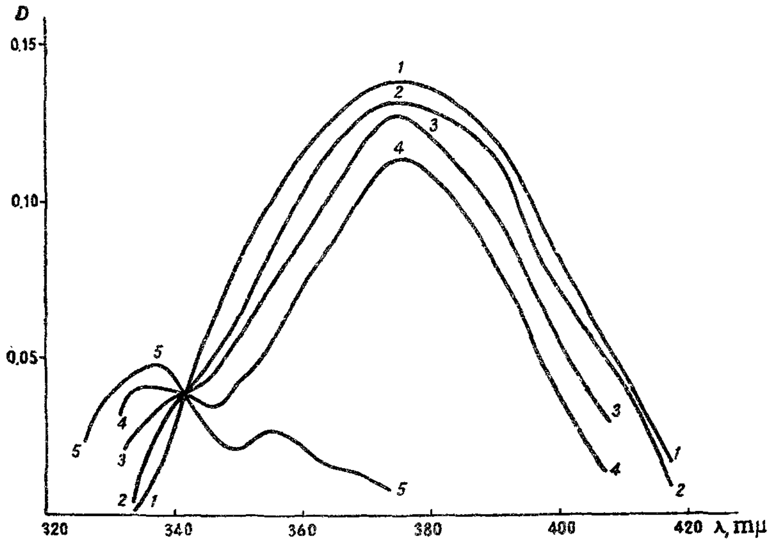

Fig. 3. Optical density curves for 2-(p-salicylalsulfanilamino)thiazole (VII) (with $1.4 \cdot 10^{-4}$ M): 1—pH 11.80; 2—pH 10.73; 3—pH 9.56; 4—pH 8.70; 5—pH 3.30.

Determination of the dissociation constant by the solubility method. The compounds to be investigated were shaken with water and NaOH solutions ($1.0 \cdot 10^{-3}$; $2.5 \cdot 10^{-3}$; $5.0 \cdot 10^{-3}$; $2.5 \cdot 10^{-2}$ and $5.0 \cdot 10^{-2}$ M) at room temperature, then centrifuged and filtered through a fine filter. The content of compound in the filtrate was determined bromatometrically [11].

Table 2

Dissociation Constants of Azomethines

Compound	Dissociation constants	
	Solubility method	Spectrophotometric method
I	$2 \cdot 10^{-10}$	—
II	$1 \cdot 10^{-10}$	$5 \cdot 10^{-10}$
III	$2 \cdot 10^{-10}$	$5 \cdot 10^{-10}$
IV	$1.6 \cdot 10^{-8}$	$0.3 \cdot 10^{-8}$
V	$1 \cdot 10^{-9}$	$0.5 \cdot 10^{-9}$
VI	—	$1 \cdot 10^{-9}$
VII	$3 \cdot 10^{-8}$	$1 \cdot 10^{-8}$
VIII	$1.2 \cdot 10^{-7}$	$0.3 \cdot 10^{-7}$
IX	$4 \cdot 10^{-7}$	—
X	$2 \cdot 10^{-8}$	—
XI	$1 \cdot 10^{-10}$	—
XII	$3 \cdot 10^{-10}$	—
XIII	$2 \cdot 10^{-8}$	—
XIV	$4 \cdot 10^{-9}$	—
XV	$2 \cdot 10^{-11}$	—

Prior experiments showed that it was possible to determine the compounds investigated bromatometrically, and the number of equivalents of $KBrO_3$ used per mole of compound under investigation. Hydrogen ion concentration was determined with a P-4 potentiometer and quinhydrone electrode, and in some of the experiments with a LP-58 laboratory potentiometer with a glass electrode.

Determination of the dissociation constant by the method of isobestic points. A SF-4 spectrophotometer was used for this. The spectra of aqueous solutions of the azomethines (about 10^{-4}M) were determined at various pHs, secured by adding various amounts of perchloric acid and NaOH. The ionic strength of the solutions, equal to 0.1, was maintained by adding $NaClO_4$ [8]. Figure 3 gives the light absorption plots of VII at different pHs. Table 2 gives the results of the determinations.

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