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NH ACIDITIES OF 7-OXO-4,7-DIHYDROPYRAZOLO- AND 1,2,4-TRIAZOLO[5,1-c][1,2,4]TRIAZINES

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The pK_a values of a number of 7-oxo-4,7-dihydropyrazolo- and 1,2,4-triazolo[5,1-c]-[1,2,4]triazines, which range from 0.33 to 6.50 and correlate with the σ meta constants of substituents in the 6 position, were determined by spectrophotometric and potentiometric methods.

Methods have been developed for the preparation of derivatives of azolo-1,2,4-triazines [1-5]; however, the literature contains no information regarding their acidic-basic properties. In this connection we have determined the ionization constants of a series of 6-R^1-7-oxo-4,7-dihydroazolo[5,1-c][1,2,4]triazines (I-XVII), for which we used spectrophotometric and potentiometric methods.

The electronic spectra of aqueous solutions of triazines I-XVII are characterized by two absorption maxima, the positions of which depend on the pH. The spectral characteristics of the compounds in the acidic (TH) and ionic (T^-) forms, as well as their ionization constants, which correspond to ionization of the NH bond of the triazine ring, are presented in Table 1. Products I, II, IV-XIII, and XV-XVII are monobasic acids, whereas carboxy derivatives III and XIV are dibasic acids. 6-Amino-7-oxo-4,7-dihydro-1,2,4-triazolo[5,1-c][1,2,4]triazine (I) displays amphoteric properties and can add a proton to the amino group. A band of vibrations of a C=O group at 1690-1720 cm^{-1} is present in the IR spectra of these compounds in the TH and T^- forms. The formation of the NH form is accompanied by a hypsochromic shift of approximately the same magnitude (Table 1). An analysis of the spectra of acid III showed that the character of the spectrum and the magnitude of the hypsochromic shift of the absorption maxima change in the same way as for the remaining compounds as the pH of the solution is changed from 7 to 4, and, consequently, pK_a 5.28 corresponds to the addition of a proton to the nitrogen atom of the triazine ring. A decrease in the pH from 3.5 to 0.5 gives rise only to a shift of the isobestic point, a certain decrease in the intensity of the absorption at 270 nm, and an increase in the intensity of the absorption at 306 nm; this makes it possible to ascribe pK_a 2.00 to dissociation of the carboxy group. In the case of 6-amino derivative I, in addition to the typical spectral changes associated with dissociation of the NH bond (pK_a 6.50), an increase in the absorption at λ_{max} of the TH form and a small bathochromic shift as a consequence of the addition of a proton to the exocyclic amino group are observed upon pronounced acidification (pH 2).

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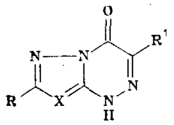
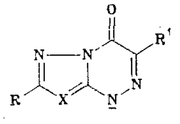
TABLE 1. Spectral Characteristics and Ionization Constants of 2-R-6-R¹-7-Oxo-4,7-dihydroazolo[5,1-c][1,2,4]triazines



TH



T⁻

Compound	R	R¹	X	pK_a[a]	λ_{max}, nm		Δλ, nm
					T⁻	TH	
I	H	NH_2	N	6,50	341 272	326 260	15 12
II	H	N-Morpholinyl	N	6,14	337 272	325 245	12 27
III	H	COOH	N	5,28[b]	324 267	306 248	18 19
IV[c]	H	H	N	4,87[b]	316 259	290 238	26 21
V	H	Cl	N	3,61[b]	326 263	300 246	26 17
VI	H	Br	N	3,61	328 265	300 248	28 17
VII	H	$COOC_2H_5$	N	2,92	330 269	309 250	21 19
VIII	H	CN	N	1,70	330 269	315 252	15 17
IX	H	NO_2	N	1,10	363 281	333 263	30 18
X	C_6H_5	Cl	N	3,62	332 255	316 244	16 11
XI	C_6H_5	Br	N	3,64	334 256	314 244	20 12
XII	C_6H_5	NO_2	N	1,10	362 259	340 254	22 5
XIII	CH_3	NO_2	N	1,32	360 281	338 264	22 17
XIV	COONa	NO_2	N	0,33	358	339	19
XV	H	NO_2	CH	2,31	391 —	371 292	20 —
XVI	CH_3	NO_2	CH	2,65	395 —	373 275	22 —
XVII	C_6H_5	NO_2	CH	2,44	394 272	371 252	23 13

[a] The accuracy in the determination was ±0.05.

[b] The following pK_a values were determined potentiometrically: 5.28 ± 0.1 for III, 4.80 ± 0.1 for IV, and 3.60 ± 0.1 for V.

[c] Compare with [6].

A satisfactory correlation of the dissociation constants with the Hammett σ meta constants was found:

$$pK_a = 5{,}34 - 5{,}26\sigma,\ r = 0{,}98,\ n = 8.$$

The introduction of a nitro group into the triazine part of the molecule has a pronounced effect on the acidity: Nitro derivatives IX and XII-XVII are strong acids that exist in the form of T⁻ anions in aqueous solutions. Compound XIV is a dibasic acid and gives a dianion in aqueous solution. A hypsochromic shift (20-30 nm) of the long-wave maximum and a decrease in the absorption intensity as compared with the anion occur in the formation of the TH forms of IX, XII, XIII, and XV-XVII. The change in the spectrum of carboxy derivative XIV differs from the changes described above. In this case only a slight hypsochromic shift (5 nm) is observed at pH from 3.5 to 1.5, and further acidification leads to an additional 19-nm hyposochromic shift and a decrease in the absorption intensity. Consequently, in this case a proton adds initially to the carboxy group (pK_a 2.40), after which a proton adds to the nitrogen atom of the triazine fragment (pK_a 0.33).

The schemes of the dissociation of carboxy-containing NH acids III and XIV differ as a result of a considerable increase in the acidity of the triazine ring under the influence of a nitro group; however, the ionization constants of the carboxy groups are close (2.00 for III, 2.40 for XIV), and the formation of an acid occurs at pH < 3.5.

Replacement of the nitrogen atom in the five-membered fragment of the investigated compounds by a CH group (XV-XVII) leads to a decrease of 1.3 pK units in the acidity.

EXPERIMENTAL

Compounds IX and XII-XVII were obtained by the method in [2], I, II, V, VI, X, and XI were obtained by the method in [7], and III, IV, and VIII were obtained by the method in [3]. The electronic spectra of aqueous solutions of the compounds were recorded with a Specord UV-vis spectrophotometer. The pH values of the solutions were measured with a pH-340 pH meter with glass and silver chloride electrodes.

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