TETRAZOLES.

10.* ACID—BASE PROPERTIES OF 5,5'-DITETRAZOLYLS

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The constants of detachment (pK_a 1.41 and 4.25) and addition (pK_{BH} −5.47 and −10.91) of protons for 5,5'-ditetrazolyl and of protonation of 1,1'-diphenyl-5,5'-ditetrazolyl (pK_{BH^+} −7.47) in aqueous solutions were determined by spectrophotometric and potentiometric methods. By comparison of the acid—base properties of the two compounds it was established that the latter exists in the trans form.

The acid—base properties of tetrazole and its simplest substituted derivatives have been studied thoroughly [1, 2]. However, no information whatsoever regarding tetrazoles with more complex structures is available. The present communication is devoted to a study of the acidities and basicities of 5,5'-ditetrazolyl and 1,1'-diphenyl-5,5'-ditetrazolyl by UV spectroscopy and potentiometric titration

5,5'-Ditetrazolyl is a dibasic N—H acid. An isobestic point is absent in the electronic spectra of 5,5'-ditetrazolyl in aqueous buffer solutions (Fig. 1), and the absorption maximum is shifted to the long-wave region as the pH is increased from 0.25 to 3.38. However, almost no changes occur in the spectra on passing to higher pH values up to 6.8. This makes it difficult to select an analytical wavelength for the determination of the pK_{a_1} value and makes it impossible to calculate the index of the second ionization constant with a sufficient degree of accuracy. In order to avoid possible errors in the determination of the pK_{a_1} value the measurements were made at 12 different pH values and at two wavelengths, viz., 205 and 210 nm. The pK_{a_1} value calculated from the experimental data was 1.41 ± 0.06. A pK_{a_2} value of 4.25 ± 0.04 was found by potentiometric titration.

It may be assumed that 5,5'-ditetrazolyl is a diacidic base, the protonation of which takes place via the scheme

$$T + H^+ \underset{}{\overset{K_{BH_1^+}}{\rightleftarrows}} TH^+ \overset{K_{BH_2^{++}}}{\rightleftarrows} TH_2^{++},$$

where T is 5,5'-ditetrazolyl. In this case the $K_{BH_1^+}$ and $K_{BH_2^{++}}$ constants can be calculated from the expressions $pK_{BH_1^+} = mH_0 + \log I$ and $pK_{BH_2^{++}} = mH_+ + \log I_+$, where H_0 and H_+ are the Hammett acidity function and the acidity function for singly charged cations, and I and I_+ are ionization ratios. The ionization ratios, which can be obtained from spectral data, are necessary for the solution of the equations. For this purpose we recorded the electronic spectra of 5,5'-ditetrazolyl in aqueous solutions of sulfuric acid with various concentrations (Fig. 2). A smooth decrease in the coefficient of molar absorption, which is associated with monoprotonation of the substrate, is observed in the UV spectra of 5,5'-ditetrazolyl as the sulfuric acid concentration is increased. Starting with 93.5% H_2SO_4, one observes a pronounced decrease in the coefficient of molar absorption; this is explained by secondary protonation of 5,5'-ditetrazolyl. Such changes in the spectra make it possible to construct the corresponding $\varepsilon-H_0$ and $\varepsilon-H_+$ dependences, which have typical S-shaped character, and to calculate the $pK_{BH_1^+}$ and $pK_{BH_2^{++}}$ values (Table 1).

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*See [1] for Communication 9.

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TABLE 1. Protonation of 5,5'-Ditetrazolyl in Aqueous Solutions of Sulfuric Acid at 25°C

H_2SO_4, %	55,2	58,8	60,4	63,5	66,3	69,3	71,0	74,7	$pK'_{BH_1^+} = mH_0 + \log I$					
$-H_0$	3,90	4,35	4,57	5,00	5,38	5,80	6,20	6,66	m	$-pK'_{BH_1^+}$	$-pK_{BH_1^+}$	r	n	s
log I*	−1,33	−1,01	−0,82	−0,50	−0,06	+0,07	0,70	1,24	0,91±0,05	4,98±0,26	5,47	0,99	8	0,12
H_2SO_4, %	95,7	96,9	97,2	98,0	98,5	98,8	99,2	99,7	$pK'_{BH_2^{++}} = mH_+ + \lg I_+$					
$-H_+$	10,11	10,30	10,36	10,51	10,64	10,74	10,94	11,20	m	$-pK'_{BH_2^{++}}$	$-pK_{BH_2^{++}}$	r	n	s
log I_+*†	−0,80	−0,55	−0,47	−0,31	−0,28	−0,14	+0,10	0,28	0,97±0,05	10,58±0,39	10,91	0,99	8	0,04

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*λ_{anal} = 205 nm, ε_B = 9000, and ε_{BH^+} = 7470.

†λ_{anal} = 220 nm, ε_{BH^+} = 8733, and $\varepsilon_{BH_2^{++}}$ = 6631.

TABLE 2. Protonation of 1,1'-Diphenyl-5,5'-ditetrazolyl in Aqueous Solutions of Sulfuric Acid at 25°C

H_2SO_4, %	74,1	75,6	77,2	79,3	80,5	81,1	83,2	85,6	$pK'_{BH^+} = mH_0 + \log I$					
$-H_0$	6,57	6,81	7,06	7,38	7,60	7,69	8,01	8,38	m	$-pK'_{BH^+}$	$-pK_{BH^+}$	r	n	s
log I*	−1,00	−0,71	−0,23	−0,12	+0,18	0,23	0,68	0,97	1,06±0,06	7,92±0,30	7,47	0,99	8	0,10

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*λ_{anal} - 280 nm, ε_B = 3170, and ε_{BH^+} = 5130.

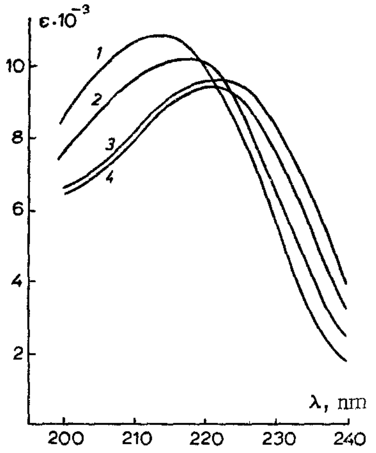

Fig. 1

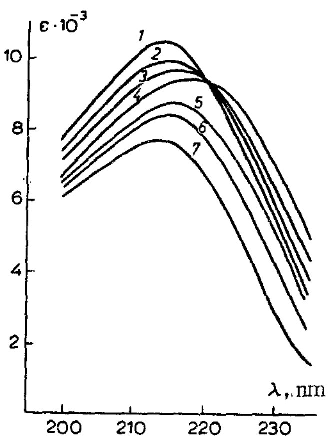

Fig. 2

Fig. 1. UV spectra of 5,5'-ditetrazolyl in aqueous buffer solutions at various pH values: 1) 0.25; 2) 1.33; 3) 3.38; 4) 6.80.

Fig. 2. UV spectra of 5,5'-ditetrazolyl in aqueous solutions of sulfuric acid (%): 1) 55.2; 2) 63.5; 3) 66.3; 4) 74.7; 5) 93.5; 6) 98.0; 7) 100.1.

It follows from the data obtained that 5,5'-ditetrazolyl is a strong dibasic acid that does not differ from oxalic acid with respect to its acidity. A comparison of the indexes of the ionization constants of tetrazole (pK_a 4.86) and 5,5'-ditetrazolyl (pK_{a_1} 1.41) provides evidence for a strong electronic interaction between the tetrazole rings in the latter. Similar principles follow from a comparison of the basicities of tetrazole (pK_{BH^+} -2.7) and 5,5'-ditetrazolyl ($pK_{BH_1^+}$ -5.5). The significant conjugation in the 5,5'-ditetrazolyl molecule can also be judged from the electronic spectra. Thus the coefficient of molar absorption (ε) of tetrazole in water is 290 (λ_{max} 206 nm), whereas $\varepsilon = 9500$ (λ_{max} 220 nm) for 5,5'-ditetrazolyl under the same conditions. On the basis of this it may be assumed that both tetrazole rings in 5,5'-ditetrazolyl are located in a single plane. However, we still do not know whether 5,5'-ditetrazolyl exists in a trans or cis conformation. An examination of three-dimenionsal models of 5,5'-ditetrazolyl does not make it possible to answer this question unequivocally. There is no doubt, however, that replacement of a hydrogen atom in 5,5'-ditetrazolyl by alkyl or aryl substituents in the trans form does not lead to disruption of the coplanarity, whereas for the cis form such changes in the structure have a substantial effect on the mutual orientation of the tetrazole rings in the molecule. Conformers with different degrees of coplanarity should obviously differ with respect to their acid–base properties. Consequently, the acidity (basicity) constants can serve as an important criterion in the evaluation of the conformation of N-substituted 5,5'-ditetrazolyl derivatives. To verify this assumption we studied the basicity of 5,5'-ditetrazolyl in aqueous solutions of sulfuric acid (Table 2).

It is apparent that 1,1'-diphenyl-5,5'-ditetrazolyl is an even weaker base than 5,5'-ditetrazolyl itself. It follows from this that a strong electronic interaction, which is possible only if the system is coplanar, exists between the tetrazole ring in the 1,1'-diphenyl-5,5'-ditetrazolyl molecule. Thus, of the two possible conformations for 1,1'-diphenyl-5,5'-ditetrazolyl, the most probable is the trans form.

Additional information (for example, the dipole moment) is necessary for the identification of the structure of 5,5'-ditetrazolyl, since this problem cannot be solved on the basis of the available data.

EXPERIMENTAL

5,5'-Ditetrazolyl and 1,1'-Diphenyl-5,5'-ditetrazolyl. These compounds were obtained by known methods. After repeated recrystallization from ethanol, the tetrazoles had characteristics that were in agreement with the literature data [3, 4]. Aqueous buffer solutions with an ionic strength of 0.01 were prepared by the method in [5]. The sulfuric acid solutions were obtained by dilution of 96% H_2SO_4 (very pure grade) with twice-distilled water;

solutions with higher concentrations were prepared by the addition of oleum (analytical grade). The concentrations were determined with an accuracy of ±0.1% by potentiometric titration with a 0.1 N solution of NaOH.

The UV spectra of the tetrazoles in buffer solutions and aqueous solutions of sulfuric acid were recorded with an SF-26 spectrophotometer with a thermostatted block (25 ± 0.1°C); the analytical concentration of the tetrazoles was $\sim 5 \cdot 10^{-5}$ mole/liter. Potentiometric titration in water was carried out with a pH-121 pH meter with a thermostatted cell (25 ± 0.1°C).

The values of the H_0 and H_+ acidity functions were taken from [6, 7]. The experimental data were processed by the methods presented in [8, 9].

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