HETEROCYCLES CONTAINING TELLURIUM AND NITROGEN.
5.* BASICITY CONSTANTS OF BENZAZOLES

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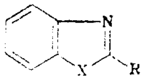
UDC 547.789.9.04

The basicities (pK_{BH^+}) of monotypically substituted 2-R-benzochalcogenazoles increase regularly on passing from benzoxazoles to benzotellurazoles.

The series of benzochalcogenazoles — benzannelated five-membered heterocycles with nitrogen atoms and group VIA elements (O, S, Se, and Te) in the 1 and 3 positions of the heterorings — has been completed by the synthesis of benzotellurazoles [2-4]. The present communication is devoted to a comparative study of the basicities of these compounds, as well as 2-(4-Y-phenyl)benzotellurazoles, and to the elucidation of the effect of the nature of group VIA elements on the change in these characteristics.



X = O, S, Se, Te; R = H, CH_3, C_6H_5, 4-YC_6H_4

Although the literature contains data on the basicity constants of analogous series of benzoxazoles [5] and benzothiazoles [5, 6], the effect of the nature of all heteroatoms X on these values has not been previously investigated. We have determined the thermodynamic basicity constants (pK_{BH^+}) of I by potentiometric titration in acetonitrile (see Table 1).

For each one of the set of substituents (H, CH_3, C_6H_5) the indexes of the basicity constants increase substantially on passing from X = O to X = Te; a sharp jump in the pK_{BH^+} values is observed on passing from benzoxazoles to benzothiazoles and from benzoselenazoles to benzotellurazoles, although the electronegativities of selenium and tellurium are very similar. There is little difference between the basicities of the selenium derivatives and the basicities of the sulfur analogs, while the benzotellurazoles are approximately three orders of magnitude more basic than the benzoxazoles and ~1.5 orders of magnitude more basic than the benzothiazoles. The effect of heteroatom X on the basicities of the azoles is determined, on the one hand, by the π conjugation of the unshared electron pair of the X atoms with the azomethine fragments of the heterocycles and, on the other, by the inductive effect of these atoms. Although the effect of π conjugation, which increases the electron density on the imino nitrogen atom, decreases on passing from O to Te, the prevailing factor is probably the inductive effect, which decreases the electron density on the nitrogen atom. The substantial decrease in the inductive effects of heteroatoms X on passing from O to Te leads to the observed regularities in the change in the pK_{BH^+} values of the benzochalcogenazoles.

Correlation of the pK_{BH^+} values of 2-(4-Y-phenyl)benzotellurazoles with the Hammett σ constants leads to $\rho = 0.978$. We calculated similar ρ constants for series of 2-(4-Y-phenyl)benzoxazoles and benzothiazoles (0.991 and 0.993, respectively) containing the same substituents Y as benzotellurazoles from the data in [5].

EXPERIMENTAL

The benzotellurazoles were synthesized by the methods presented in [3, 4]; the remaining azoles were obtained by known methods.

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*See [1] for Communication 4.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 836-837, June, 1991. Original article submitted December 22, 1989.

TABLE 1. Indices of the Thermodynamic Basicity Constants of I in Acetonitrile at 25°C

X	R	pK_{BH^+}	X	R	pK_{BH^+}
O	H	5,70	O	C_6H_5	(6,03 [5])
S	H	7,87	S	C_6H_5	7,24
		(7,84 [6])			(7,16 [5, 6])
Se	H	8,03	Se	C_6H_5	7,46
O	CH_3	7,30	Te	C_6H_5	8,67
S	CH_3	8,63	Te	4-ClC_6H_4	8,36
		(8,67 [6])	Te	4-BrC_6H_4	8,35
Se	CH_3	8,87	Te	4-$CH_3C_6H_4$	9,20
Te	CH_3	10,10	Te	4-$CH_3OC_6H_4$	9,60

The ionization constants of the conjugate acids of bases I were determined in acetonitrile by the method presented in [7].

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