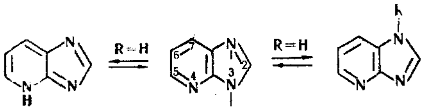
LETTERS TO THE EDITOR

TAUTOMERISM OF IMIDAZO[4,5-b]PYRIDINE

Yu. M. Yutilov, N. R. Kal'nitskii,
and R. M. Bystrova

UDC 541.625:547.821'781:543.422.6

The prototropic tautomerism of imidazo[4,5-b]pyridine (I) has not been previously studied. On the strength of the electronic asymmetry of I, one of its three possible tautomeric forms (IIa, IIIa, IV) should dominate, as in the case of purine [1], which has the structure of the 9H-form.



IV

II,IIIa R=H; II,III b R=CH_3

Although the UV spectrum of I is similar to the spectrum of model compound IIb, the difference in the character of the absorption of the latter and of the second model structure (IIIb) is not great enough to draw positive and unambiguous conclusions relative to the predominance of one or the other tautomeric form in solution.

More definite results can be obtained in a study of the dipole moments of I and its N_1- and N_3-methyl derivatives (Table 1). The experimental values of the dipole moments of fixed tautomeric forms IIb and IIIb are in satisfactory agreement with the calculated values (the data in [3,4] were used in the calculation). At the same time, the experimentally obtained moment for I is 1.99 D, i.e., close to the dipole moment of 3-methylimidazo[4,5-b]pyridine and markedly different from the dipole moment of the 1-methyl isomer. Considering that the theoretical dipole moment of quinoid form IV that we calculated is about 6 D, it can be assumed that imidazo[4,5-b]pyridine exists primarily in the 3H-form (IIa) in benzene.

LITERATURE CITED

1. A. Bendich, P. Russell, and J. Fox, J. Am. Chem. Soc., 76, 6073 (1954).
2. Y. Mizuno, M. Ikehara, T. Itoh, and K. Saito, J. Org. Chem., 28, 1837 (1963).
3. L. E. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, Trans. Faraday Soc., 47, 113 (1951).
4. O. A. Osipov and V. I. Minkin, Handbook of Dipole Moments [in Russian], Moscow (1965).

TABLE 1. UV Spectra and Dipole Moments of the Investigated Compounds

Compound	UV spectrum, λ_{max}, nm ($\log \varepsilon$) (in alcohol)	μ, D (benzene)	
		expt.	calc.
I ≡ II a	244(3,56); 282(3,97); 288(3,88)	1,99	—
II b	252(3,72); 284(4,02)[2]	1,85†	1,67
III b	240(3,39); 252(3,66); 282(4,10); 290(3,98)*	5,78	5,77

*Inflection.

† In hexane, 1.70 D.

L. V. Pisarzhevskii Donetsk Physical-Organic Chemistry Branch, Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, p. 1436, October, 1971. Original article submitted December 30, 1970.