prove useful for the study of natural ribonucleic acids.[10]

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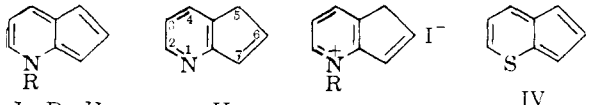
THE TAUTOMERISM OF 5H-1-PYRINDINE

Sir:

Recently much interest[1] has centered on heterocyclic analogs of azulene, which were first described forty years ago by Armit and Robinson.[2] Such compounds are iso-π-electronic with azulene with the heteroatom (N, O, S) providing an electron pair instead of a (—CH=CH—) group; they are expected to resemble azulene in their ultraviolet and visible absorption spectra and general aromatic properties. We wish to report evidence for the existence of the parent pseudo-azulene[3] of the pyrindine group discussed by Armit and Robinson,[2] namely, 1H-1-pyrindine (Ia).



Ia, R = H
b, R = Me

II

IIIa, R = H
b, R = Me

IV

Robison[4] prepared 5H-1-pyrindine (II) and noted that the freshly distilled liquid had an orange color which was discharged on dilution with organic solvents, and that a 10^{-4} *M* solution in cyclohexane was completely transparent above 305 mμ. This color was also discharged slowly by freezing the material. Anderson, *et al.*,[5] suggested that the color was due to the presence of the tautomeric pseudoazulene (Ia).

We have confirmed Robison's observations and have obtained spectral evidence which suggests that the orange color of (II) is indeed due to the presence of (Ia). Pyrindine (II) was left overnight at room temperature with a large excess of methyl iodide. The residue, obtained by evaporation of the excess methyl iodide, was crystallized from methanol to give cream colored crystals (50%) of pyrindine methiodide (IIIb), m.p. 248-250° (dec.). *Anal.* Calcd. for $C_9H_{10}IN$: C, 41.69; H, 3.86; N, 5.41. Found: C, 41.30; H, 3.60; N, 5.27. A dark orange oil of 1-methyl-1-pyrindine (Ib) was obtained by treating (IIIb) with alkali; this material could not be isolated as it was converted rapidly into an infusible solid, insoluble in organic solvents. In this way it resembled its sulfur analog[6] (IV) and differed from the more stable pseudoazulenes prepared by Anderson, *et al.*[5] However, its ultraviolet and visible spectrum was obtained by treating pyrindine methochloride (obtained by passing an aqueous solution of (IIIb) through a Dowex 1 chloride column) with alkali: $\lambda_{max.}^{0.1\,N\,NaOH}$ 220, 256, 320, 456 mμ (log ϵ = 3.53, 4.06, 3.56, 2.84). The spectrum was recorded rapidly as (Ib) readily decomposed in aqueous solution, even at pH 8.

Figure 1 shows the visible absorption spectrum of (Ib) with a thousand-fold reduced ϵ scale and that of the colored impurity in *neat* pyrindine with full ϵ scale. Despite the different solvents, the two absorption bands are strikingly similar; they have $\epsilon_{max.}$ values of 685 and 0.76, respectively. If it is assumed that N-methylation of (Ia) does not alter the $\epsilon_{max.}$ of its visible band appreciably, then at 20° 5H-1-pyrindine (II) contains 1.1 parts per 1000 of the colored pseudoazulene tautomer (Ia) in equilibrium with it. This equilibrium can be shifted by dilution or freezing. It is noteworthy that N-methylation causes a hypsochromic shift of 14 mμ, but this may be due to the different solvents involved.

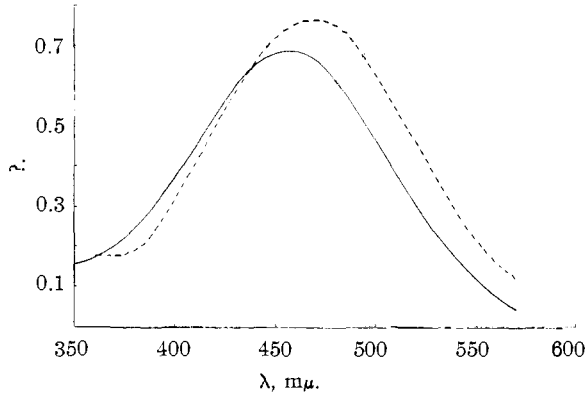


Fig. 1.—Full curve is for 1-methyl-1-pyridine (Ib) in 0.1 *N* NaOH; ordinate, 10^{-3} ϵ value. Broken curve is for neat 5H-1-pyridine at 20°; ordinate, ϵ value.

This estimate of approximately 0.1% of pseudoazulene (Ia) in tautomeric equilibrium with (II) has been confirmed by pK_a measurements. The latter compound has pK_a 5.7 (determined potentiometrically) whereas (Ib) has pK_a 8.7 (determined spectroscopically[7]). If (Ia) is assumed to have the same pK_a as (Ib) (ΔpK_a for N-methylation is normally[8] about 0.2 unit), and if both tautomers (Ia) and (II) are assumed to have the same conjugate acid (IIIa), then it follows[8] that the tautomeric equilibrium constant is 10^3 in favor of (II). Tautomerism between (II) and the other possible 2,3-cyclopentenopyridine, 7H-1-pyrindine has not been investigated. Comparison of the ultraviolet spectra of (II), 2-vinyl-[9] and 3-vinylpyridine[10] was not helpful.

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(1) See, for example, D. Leaver, J. Smolicz and W. H. Stafford, *J. Chem. Soc.*, 740 (1962).

(2) J. W. Armit and R. Robinson, *J. Chem. Soc.*, 827 (1922).

(3) Term originated by R. Mayer, see reference (6).

(4) M. M. Robison, *J. Am. Chem. Soc.*, **80**, 6254 (1958).

(5) A. G. Anderson, Jr., W. F. Harrison, R. G. Anderson and A. G. Osborne, *ibid.*, **81**, 1255 (1959).

(6) R. Mayer, *Angew. Chem.*, **69**, 481 (1957); R. Mayer, J. Franke, V. Horák, I. Hanker and R. Zahradník, *Tetrahedron Letters*, No. 9, 289 (1961).

(7) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co., Ltd., London, 1962, pp. 69–92.

(8) S. J. Angyal and C. L. Angyal, *J. Chem. Soc.*, 1461 (1952).

(9) D. W. Adamson, P. A. Barrett, J. W. Billinghurst and T. S. G. Jones, *ibid.*, 2315 (1957).

(10) M. L. Swain, A. Eisner, C. F. Woodward and B. A. Brice, *J. Am. Chem. Soc.*, **71**, 1341 (1949).