

The Tautomerism of 2-Amino-5-nitrosotropone

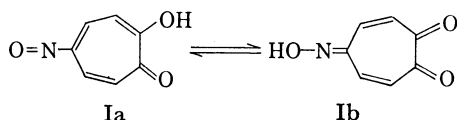
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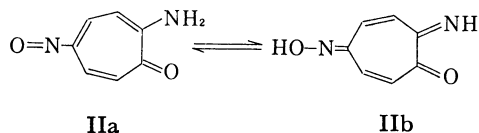
Synopsis. It was confirmed that 2-amino-5-nitrosotropone (II) exists in its tautomeric form (IIb) by the measurement of its dissociation constant and UV spectra.

Previously, it was established¹⁾ that the methylation of 5-nitrosotropolone (I) with diazomethane does not give its methyl ether, while its acetylation and benzoylation afforded, respectively, the corresponding acetate and benzoate of tropononemonoxime (Ib).



In the course of measurements²⁾ of the dissociation constants of several 4-, 5-, and 6-substituted 2-aminotropones, 2-amino-5-nitrosotropone (II) was found to show an extremely larger pK_a value (5.68) than those of other 2-aminotropones.

In order to reveal these differences between 2-amino-5-nitrosotropone (II) and other 2-aminotropones, we assumed its tautomeric form (IIb), which is similar to Ib, and compared II with 5-nitrosotropolone (I).



Experimental

Materials. 5-Nitrosotropolone (I) was prepared by the nitrosation of tropolone,^{1,3)} while 2-amino-5-nitrosotropone (II) was obtained by its ammonolysis.¹⁾

Measurement of Dissociation Constants. The dissociation constants were measured spectrophotometrically in 50% aqueous methanol at 20 °C using the method of Albert and Serjeant.⁴⁾

The absorption spectra were taken on a Hitachi spectrophotometer (EPS-3T), and the pH values were measured by means of a Hitachi-Horiba pH meter (F-5).

Results and Discussion

The dissociation constants are listed in Table 1. In spite of the strong electron-withdrawing effect of the nitroso group, the pK_a value of 2-amino-5-nitrosotropone (II) is remarkably larger than those of other 2-aminotropones [pK_a =2.63 (5-methyl) to 1.34 (5-

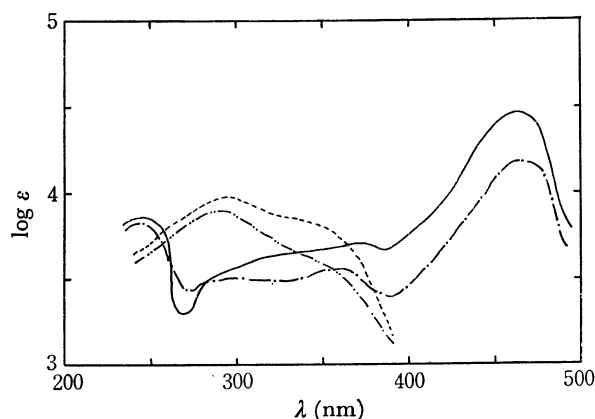


Fig. 1. The UV spectra of 5-nitroso compounds

I: — pH 7.30, ---- pH 1.31

II: pH 7.52, -.-.- pH 1.89

TABLE 1. DISSOCIATION CONSTANTS

Compound	pK_a
I	5.63
II	5.68

chloro)]²⁾ and is close to the pK_a value of 5-nitrosotropolone (I).

Furthermore, the two 5-nitroso-substituted compounds (I and II) show very similar spectral patterns in both acidic and basic media, as is shown in Fig. 1.

Consequently, it was revealed that 2-amino-5-nitrosotropone (II) exists also in the tautomeric structure (IIb). It is thought that the pK_a values of I and II are due to the dissociation of the OH group in the oxime form.

In addition, it is known⁵⁾ that *p*-nitrosophenol, which exists in similar tautomers, shows a lower pK_a value (6.36) than do other phenols [pK_a =10.26 (*p*-methyl) to 7.15 (*p*-chloro)].

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References

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