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The Tautomerism of 2-Amino-5-nitrosotropone

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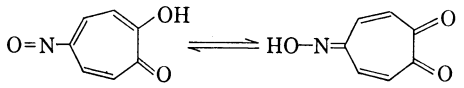
Synopsis. It was confirmed that 2-amino-5-nitrosotropone (II) exists in its tautomeric form (IIb) by the measurement of its dissociation constant and UV spectra.

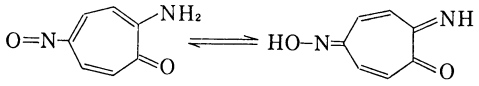
Previously, it was established[1] that the methylation of 5-nitrosotropolone (I) with diazomethane does not give its methyl ether, while its acetylation and benzoylation afforded, respectively, the corresponding acetate and benzoate of tropoquinonemonoxime (Ib).



Ia Ib

In the course of measurements[2] 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).



IIa IIb

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

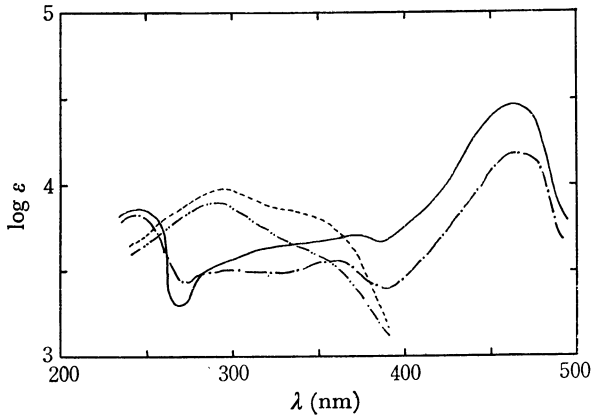


Fig. 1. The UV spectra of 5-nitroso compounds
I: —— pH 7.30, ------ pH 1.31
II: ····· pH 7.52, -·-· pH 1.89

Table 1. Dissociation constants

Compound	pK_a
I	5.63
II	5.68

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 known[5] 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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