

NMR Spectroscopic Studies on the Tautomerism in Schiff Bases of Tenuazonic Acid Analogs

TABLE 2. CHEMICAL SHIFTS OF ACTIVE HYDROGENS

to the B_N form, and the lower one to the C_N form.

The observed spectra of the other compounds showed patterns similar to that of IA and indicated the same conclusion in the assignment of the signals. However, the observed ^{15}N -H coupling constant (86.4 Hz) of the C_N form in the Schiff base (III) of 3-acetylthio-tetronic acid is found to be markedly smaller than the values for the others. This suggests that *ca.* 5% of the C_O form is present at 34 °C in the CDCl_3 solution of this compound. The presence of the C_O form in III is also supported by the results for the ^{13}C -NMR spectrum of III, which showed an additional small signal of enolic carbon at 193.88 ppm (from TMS) besides two signals at 195.18 and 198.81 ppm arising from free carbonyl carbon and hydrogen-bonded carbonyl carbon respectively. The exceptional feature of III could be explained by the geometry of the molecule. Simple molecular orbital calculation are in progress to obtain further insights in this field.

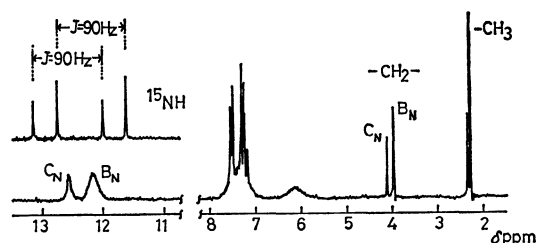


Fig. 1. NMR spectrum of 3-(1'-anilinoethylidene)-pyrrolidine-2,4-dione (IA) in CDCl_3 at 90 MHz.

Experimental

Materials. The IA,⁷⁾ IB,⁷⁾ II,⁸⁾ and III⁹⁾ were prepared according to the procedures described in the literature cited. Aniline- ^{15}N (95% isotopic purity) was obtained from Prochem BOC, Ltd.

Measurements. The NMR spectra were measured with a Hitachi Perkin-Elmer R-22 spectrometer at 90 MHz at 34 °C,

using TMS as the internal standard. Solutions were made so as to contain 1.5×10^{-4} mol of compounds in 0.4 ml of CDCl_3 .

The ^{13}C -NMR spectra measured on a JNM-FX60 spectrometer equipped with a PFT-100 Fourier transform accessory at 25.1 MHz, using TMS as the internal reference and a 10-mm-diameter NMR tube. The spectra were obtained by 5000-times accumulations measured on a broad-band proton decoupler. The solution contained 200 mg of the sample in 2 ml of CDCl_3 .

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References

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- 2) Common names were consciously introduced for these compounds in order to express the mixed systems of complicated tautomers.
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