

## A Diquaternary Salt of 1,5-Naphthyridine

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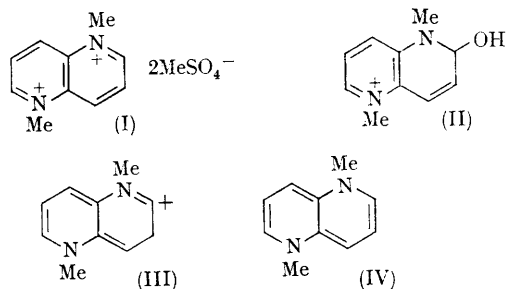
IN connection with our study<sup>1</sup> of diquaternary salts related to bipyridylum herbicides, we have prepared the first example of a diquaternary salt of a naphthyridine.

1,5-Naphthyridine was heated under reflux in dimethyl sulphate for 1 hr. The brown solution was allowed to cool and was then diluted with dry ethanol. The grey solid which precipitated was crystallized from aqueous ethanol to afford 1,5-dimethyl-1,5-naphthyridinium dimethosulphate (I), m.p. 200° (decomp.) in 33% yield. The structure was confirmed by elemental analyses and by the n.m.r. spectrum† (D<sub>2</sub>O) which consisted of singlets at  $\delta = 3.7$  p.p.m. (6 methosulphate protons) and 4.95 (6 N-Me protons), a quartet at 8.65–8.9 (assigned to the protons at positions 3 and 7) and a signal which appears as a triplet at 9.7–9.9 attributed to the remaining four aromatic protons.

The diquaternary salt in aqueous solution is in reversible equilibrium with another species, presumably the pseudo-base (II). At pH values lower than about 5.0 the predominant form is (I), the u.v. spectrum in water at pH 0.8, for example, showing maxima at  $\lambda$  270, 311, and 323  $m\mu$  ( $\log \epsilon$  3.79, 3.91, and 4.01). At pH 8.0 the maxima are at 270 and 377  $m\mu$  ( $\log \epsilon$  4.01 and 3.83). At intermediate pH values the spectrum shows the maxima of both species.

Compound (I) in aqueous solution on treatment with zinc dust or sodium dithionite gave an intensely green solution, the coloration being attributed to the radical cation of which (III) is

one canonical form. The presence of a high concentration of a free radical species was confirmed by the observation that the green solution gave essentially no n.m.r. spectrum apart from the signal due to the methosulphate protons. On polarographic examination at pH 2.7, 3.5, and 4.3 in Britton and Robinson buffers, compound (I) gave two symmetrical one electron reduction steps with half-wave potentials ( $E_0$ ) of +0.02 and -0.33 volts, independent of pH and concentration, attributed to the formation of (III) and presumably (IV) respectively. At higher pH values, the wave heights decreased in size, and disappeared above pH 8.0. Simultaneously a reduction wave appeared at a much lower potential ( $\sim -0.80$  volts). The radical cation (III) is stable for several minutes in presence of zinc powder but is unstable in air when the reducing agent is removed.



(Received, October 3rd, 1967; Com. 1052.)

† Sodium 3-trimethylsilyl-1-propanesulphonate was the internal reference.

<sup>1</sup> L. A. Summers, *Nature*, 1967, **214**, 381; L. A. Summers and V. A. Pickles, *Chem. and Ind.*, 1967, 619.