

Stable Radical Cation from a Diquaternary Salt of 2,2'-Biquinoline.

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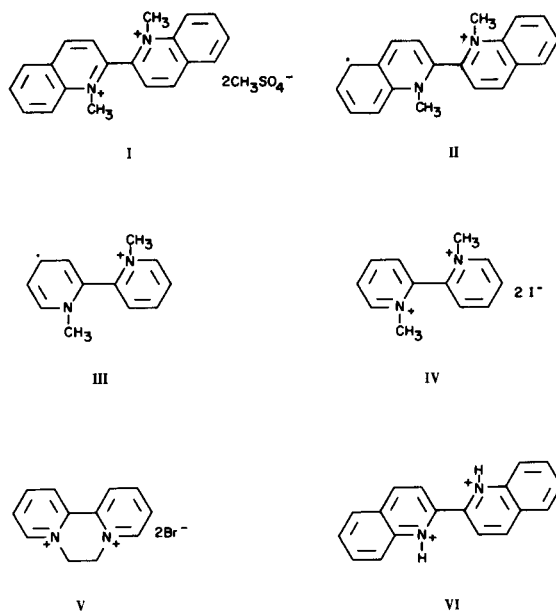
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There has been much interest recently in radical cations (1-7) derived by the one electron reduction of diquaternary salts of heteroaromatic systems such as 2,2'-bipyridine, 1,10-phenanthroline and 1,5-naphthyridine. We now report the preparation of a stable radical cation from a diquaternary salt of 2,2'-biquinoline.

1,1'-Dimethyl-2,2'-biquinolinium dimethosulphate (I) was prepared from 2,2'-biquinoline by use of dimethyl sulphate but attempts to obtain corresponding salts using methyl iodide, 1,2-dibromoethane and 1,3-dibromopropane were unsuccessful. The salt (I), as expected, was soluble in water and was stable in aqueous solution below about pH 10.5. On treatment of an aqueous solution of I with zinc dust an intense violet-red coloration developed immediately, which is attributed to the radical cation of which II is one canonical form. The presence of a high concentration of a stable radical was confirmed by nmr spectroscopy, the red solution giving essentially no spectrum apart from the signal due to the methosulphate protons. This suggests that the odd electron is delocalised over all positions of the quinoline rings. When the reducing agent was removed and the solution was shaken in air the deep color rapidly discharged. The nmr spectrum and integral ratios obtained then were almost identical with those of the original salt indicating that the one electron transfer is essentially completely reversed by air.

Polarographic examination confirmed the uptake of one electron by I, which gave a symmetrical one electron reduction wave in the pH range 2.2 - 9.9 with a half-wave potential of -0.25 volts, against a normal hydrogen electrode, independent of pH. There was no clearly defined second reduction wave. The current gradually increased as the applied voltage decreased.

The stability of the radical cation (II) and the reversibility of the one electron transfer contrast with the relative instability (8) of the radical cation (III) derived from 2,2'-bipyridine dimethiodide (IV). In IV the two pyridine rings are considered to be twisted out of a plane because of the steric effects of the methyl groups ortho to the central bond (9). Consequently the radical cation (III) is less stable than radical cations derived from essentially planar (10) molecules such as 6,7-dihydrodipyrido[1,2-*a*:2',1'-*c*]-pyrazinediium dibromide (V). Likewise, ultraviolet spectral evidence indicated that the diquaternary salt (I), λ_{max} 247 and 329 μ , is less conjugated than the di-cation (VI), λ_{max}



max 270 and 357 μ . The latter values agree with those reported by Linnell and Kaczmarczyk (11). The larger number of possible canonical forms available to the polynuclear radical cation (II) compared with III are apparently sufficient to enhance considerably its stability. The bulkiness of the two quinoline nuclei which presumably hinders rotation about the central bond may also be a contributing factor.

The salt (I) with its redox potential of -0.25 volts provides an extension to the range of redox indicators of the viologen type (12) which so far have been confined to potentials below -0.32 volts (7) (13) (14).

Certain diquaternary salts of bipyridines, for example the salt V, show considerable herbicidal activity (7) but the salt I, when tested as a post-emergence herbicide at 8 lbs/acre on six plant species was inactive. The lack of phytotoxicity shown by I is probably due to its large size (2).

EXPERIMENTAL

Britton and Robinson buffers were used in the polarography experiments, which were conducted at 20° with a standard calomel electrode and 0.001M solutions. Half-wave potentials are assumed to be E_0 values and were calculated by adding 0.25 volts to the

$E_{1/2}$ values. Nmr spectra were determined for 10% w/v solutions in deuterium oxide at 60 Mc/sec with sodium 3-trimethylsilylpropane-1-sulfonate as internal standard. Similar solutions were used for the zinc powder reduction experiments. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

1,1'-Dimethyl-2,2'-biquinolinium Dimethosulphate (I).

2,2'-Biquinoline (1 g.) was refluxed for 1 hour with dimethyl sulphate (10 ml.) and the mixture cooled. The solution was poured into cold dry ethanol (100 ml.) and the solid which precipitated was crystallised from aqueous ethanol to give off-white crystals of the diquatery salt m.p. 260° dec. (yield 50%). The analytical figures, obtained after drying 1 hour *in vacuo* at 100°, indicated the presence of 0.5 mole of ethanol of crystallisation.

Anal. Calcd. for $C_{22}H_{24}N_2O_8S_2 \cdot 0.5 C_2H_5OH$: C, 52.0; H, 5.1; N, 5.3; S, 12.1. Found. C, 52.3; H, 5.0; N, 5.2; S, 12.2.

The nmr spectrum (deuterium oxide) showed singlets at δ 3.65 ppm (6 methosulphate H) and 4.6 (6 *N*-methyl H), a complex multiplet at 8.15-8.8 (10 aromatic H), and a doublet at 9.55-9.7 (2 aromatic H). The nmr spectrum also showed signals corresponding to ethanol of crystallisation. The ultraviolet spectrum in water, pH 6 and 94% sulphuric acid showed λ max 247 m μ ($\log \epsilon$ 4.90) and 329 (4.30).

The ultraviolet spectrum of 2,2'-biquinoline, taken in 94% sulphuric acid to obtain the di-cation (VI), agreed with that reported previously (11).

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