Structure of Alleged Dipyrido[1,2-*a*:1′,2′-*d*]pyrazinium Dibromide: 6,12-Dihydro-6-hydroxydipyrido[1,2-*a*:1′,2′-*d*]pyrazinium Dibromide

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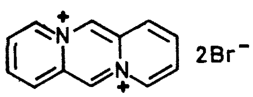
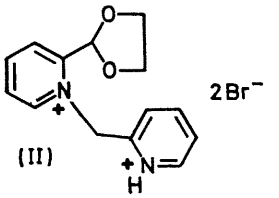
Summary The compound previously thought to be dipyrido[1,2-*a*:1′,2′-*d*]pyrazinium dibromide is in fact 6,12-dihydro-6-hydroxydipyrido[1,2-*a*:1′,2′-*d*]pyrazinium dibromide.

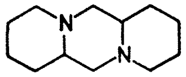
THE aromatic diquaternary system (I) has been reported[1] to be formed by the cyclisation of (II) with hydrobromic acid. The evidence for the formation of (I) rested largely on elemental analyses of the product which corresponded to a monohydrate of (I) and on hydrogenation of the product to the perhydro-base (III). The u.v. spectrum in water (pH not specified), λ_{max} 199, 262, 448 nm (log ϵ 4·03, 3·94, 2·97), seemed to us to be unlikely for structure (I) in view of the spectrum recorded[2] for the related salt (IV), λ_{max} 242, 361, 379, 399 (4·68, 3·99, 4·01, 3·93).



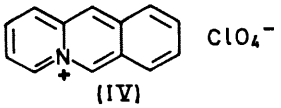
(I)



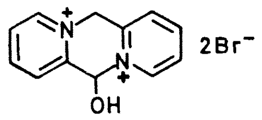
(II)



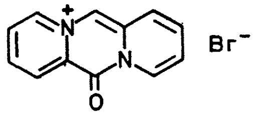
(III)



(IV)



(V)



(VI)

On repeating the synthesis,[1] we obtained a product essentially identical in physical properties† with the compound reported to be (I). Its n.m.r. spectrum however was inconsistent with structure (I) but was in accord with the hydroxy-structure (V). The spectrum‡ in CF_3CO_2H showed a quartet at δ 6·35—7·03 p.p.m. (assigned to the methylene protons), a singlet at 7·85 (C*H*–OH), and a complex multiplet at 8·14—9·57 (8 aromatic protons). In D_2O the methylene protons were exchanged rapidly for deuterium and the methine proton more slowly. (*cf.* ref. 3). The formation of (V) from (II) is analogous to the synthesis of corresponding hydroxy-derivatives in related 2,2′-bipyridyl[4-6] and 1,10-phenanthroline[7] series. The formation of the perhydro-base (III) from (V) also finds analogy in similar conversions.[5] The salt (V) is readily oxidised (*cf.* ref. 1) to the amide salt (VI). The salt (V) is stable in aqueous solution below about pH 3, the u.v. spectrum at pH 1·5, for example, showing λ_{max} 262 (4·05). Above pH 3 it gradually breaks down to a mixture of unidentified products, probably including the amide (VI), λ_{max} 261, 308, 321, 451 (3·87, 2·85, 2·81, 4·65) (*cf.* refs. 1, 8). These break-down products account for the long wavelength absorption maximum at λ 448 reported in the spectrum of (V) in water.[1] So far, attempts to dehydrate (V) to (I) have not been successful.

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† M.p., u.v. spectrum in distilled water, pH 5·5, and elemental analyses.

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

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