

STRUCTURE OF A DIHYDROQUINALDINE DIMER FROM ELECTROLYTIC REDUCTION

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REDUCTION of quinaldine in acid solution either by zinc metal or at a mercury cathode results in the formation of a dimer of dihydroquinaldine ($C_{20}H_{22}N_2$, m.p. 181-182°).¹ Electrolytic reduction of quinaldine in alcoholic potassium hydroxide was reported by Levchenko give an isomeric dimer, m.p. 119-120°.² We originally attempted to prepare Levchenko's dimer in order to investigate its structure, but under the conditions for electrolysis that we employed we obtained none of the dimer of m.p. 119°, but one of the products isolated consistently was a compound of m.p. 138-140° that is assigned structure I.

The formation of the dimer (I, m.p. 138-140°) occurs with the uptake of one mole of hydrogen per mole of dimer [Found: C, 83.01; H, 6.80; N, 9.70; M. W. (Rast) 330. $C_{20}H_{20}N_2$ requires: C, 83.29; H, 6.99; N, 9.71; M. W. 288].³ The dimer is unsaturated and absorbs one mole of hydrogen catalytically to afford a more stable tetrahydroquinaldine dimer [II, m.p. 133-134°; Found: C, 82.77, 82.63; H, 7.79, 7.80; N, 9.66, 9.54; M. W. 261 (isothermal distillation in $CHCl_3$). $C_{20}H_{22}N_2$ requires: C, 82.76; H, 7.58;

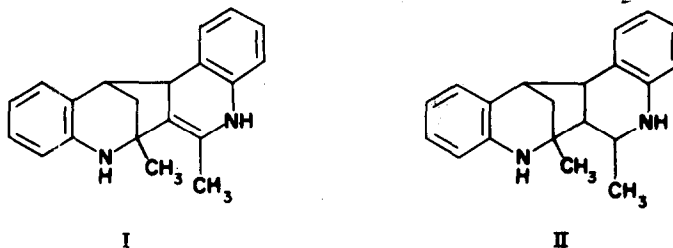
¹ G. Heller, Ber. Dtsch. Chem. Ges. 47, 2893 (1914); H.C. Dunathan, I.W. Elliott and P. Yates, Tetrahedron Letters 781 (1961).

² V.V. Levchenko, J. Gen. Chem. (U.S.S.R.) 18, 1245 (1948); Chem. Abstr. 43, 955 (1949)

³ Quinaldine in 10 per cent alcoholic potassium hydroxide was reduced at a mercury cathode at 8 V and current density 5.3 A/cm² for 4 hr at 15°C. The cathode was stirred magnetically, and the anode compartment was separated by a porous thimble. The work-up procedure was that described by Levchenko².

N, 9.66; M. W. 290].

The structural formulations I and II for the dihydro- and tetrahydro-quinaldine dimers respectively are based on the following points of evidence. The dimer (I) is a diacidic base, forming a di-perchlorate, m.p. 220-221°



(Found: C, 48.78; H, 5.10; N, 5.69. $C_{20}H_{22}Cl_2O_8 \cdot \frac{1}{2}H_2O$ requires: C, 48.59; H, 4.69; N, 5.67). Other similar salts are prepared from I and II.

The ultraviolet spectrum of the dimer [I: λ_{max}^{EtOH} 252 m μ (log ϵ 2.97), inflection at 295 m μ (log ϵ 2.50); λ_{min} 236 m μ (log ϵ 2.81)] allows a 1,4- or 3,4-dihydroquinoline ring, in addition to a 1,2,3,4-tetrahydroquinoline, but excludes a 1,2-dihydroquinoline system.⁴ In the infrared region the dimer (I) has a medium intensity band at 3.05 μ attributed to N-H stretching vibrations and a band at 6.05 μ that disappears on hydrogenation of I to II. Further evidence that the band at 6.05 μ can be assigned to the double bond in the 2,3-position of one quinaldine ring is gained from the observation that when the base (I) is converted to the perchlorate this band is replaced by one at 5.91 μ . This behavior is characteristic of enamine-iminium changes reported by Leonard and by Witkop⁵.



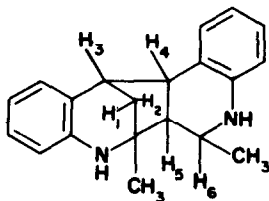
The NMR spectra of the dimer (I) and its dihydro derivative (II) have

⁴ I.W. Elliott and P. Yates, *J. Org. Chem.* **26**, 1287 (1961).

⁵ N.J. Leonard and V.W. Gash, *J. Amer. Chem. Soc.* **76**, 2781 (1954);
B. Witkop, *Ibid.* **78**, 2873 (1956).

been recorded.⁶ The experimental sample of II provided the better spectrum for detailed analysis although the NMR data for I corroborate all assignments.

The spectrum of II reveals that there are a total of 22 hydrogens present. These are grouped into the eight aromatic hydrogen signals, a group of five signals around $\tau = 7.8$, and the two methyl groups of six hydrogens around $\tau = 8.6$. The latter consists of a doublet signal flanking $\tau = 8.6$ and a tall single peak at $\tau = 8.5$, indicating the presence of one secondary and one tertiary methyl group.



II a

The details of the spectra are consistent with structure IIa (arbitrarily numbered) and are summarized in Table 1. The two N-H peaks are part of the band pattern around $\tau = 6.6$

TABLE 1

Hydrogen	τ -Values	Coupling constants
H ₄	6.25	$J_{4,5} = 12$ cps $J_{4,3} = 6$ cps
H ₆	6.63	$J_{6,5} = 5$
H ₃	7.01	$J_{3,1} = 4$ $J_{3,2} = 1$
H ₅	7.65	$J_{5,4} = 12$ $J_{5,6} = 5$
H ₁ , H ₂	7.92, 7.97	$J_{1,2} = 12$ $J_{1,3} = 4$ $J_{2,3} = 1$

⁶ We thank Dr. LeRoy F. Johnson, Applications Laboratory, Varian Associates for these measurements and interpretations. The samples were run in deuterio-chloroform, and peak positions are discussed in terms of the τ -values relative to tetramethylsilane as internal standard.

From a comparison with the NMR spectrum of I it is evident that the non-aromatic double bond is between the carbon atoms that were holding H₅ and H₆ in IIa. This is demonstrated by the absence of a peak in the vinyl hydrogen region and by the disappearance of the peak for the secondary methyl group together with the appearance of a new peak at $\tau = 7.8$, characteristic of a methyl group on a double bond.

Some reactions of the dimer and the stereochemistry of I and II will be discussed in the detailed paper.

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