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SYNTHESIS AND CHARACTERIZATION OF A NITROGEN-BRIDGED DIAZANAPHTHOQUINONE[1]

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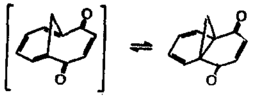
Current interest in potentially aromatic ten π-electron cycles of 1,6-bridged[10]annulenes (I)[2] and in particular, of the 2,5-quinone derivatives(II)[3] promts us to report the synthesis of diazanaphthoquinone (V), a fused 6/6 ten π-electron aza-aromatic ring system with two bridged nitrogen atoms.

(I)



(IIa) (IIb)

Bromination of butadiene-diazaquinone adduct (III)[4] in CH_2Cl_2 at -78° gave the dibromo compound (IV) in 87% yield; mp 159-162°, $C_8H_8N_2O_2Br_2$,* $\tau(CDCl_3)$ 3.2 (s, 2H), 5.6 (m, 6H), ν_{max} (KBr) 1643 cm^{-1} (C=O). Treatment of compound (III) with DBN (1,5-diazabicyclo[4.3.0]non-5-ene) in refluxing benzene afforded orange needles (V) in 19% yield; mp 149-152°, $C_8H_6O_2N_2$,* ν_{max} (KBr) 1624 cm^{-1} (C=O). However, the reaction did not proceed with triethylamine or t-BuOK. The N.M.R. spectrum of the orange product shows two double doublet signals at τ 2.19 (2H) and 4.10 (2H) with coupling constants of 3.0 and 6.0 Hz, and a sharp singlet at τ 2.93 (2H), suggesting the presence of a diamagnetic ring current within the molecule. Furthermore, the U.V. spectrum [λ_{max} (MeOH) 214 nm (ε 13,100), 411 (6,500, shoulder), 437 (7,300), 467 (5,700)] indicates the presence of the π-conjugated ring system (see Figure 1).

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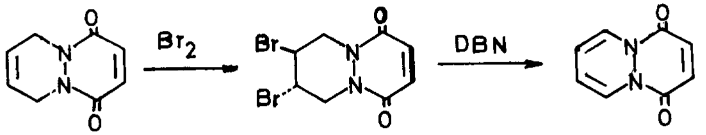
* All new compounds gave satisfactory analytical results for the proposed structures.



(III) (IV) (V)

Since the N.M.R. spectrum shows no change when a solution in deuteriochloroform is cooled to -20°, the possibility that the structure (VI) might be in a rapid equilibrium with diaza-annulenone system is ruled out. Thus, the compound might be more properly represented by bicyclic diazanaphthoquinone(pyridazino[1.2-a]pyridazine-1,4-dione)(V) as an aromatic ten π-electron system rather than monocyclic diazaannulenone (VI). In this connection, however, two types of nitrogen-bridged annulene derivatives such as compounds VII[5] and VIII[6] have been reported. Studies in progress are aimed at finding answers to these questions in these ring systems.

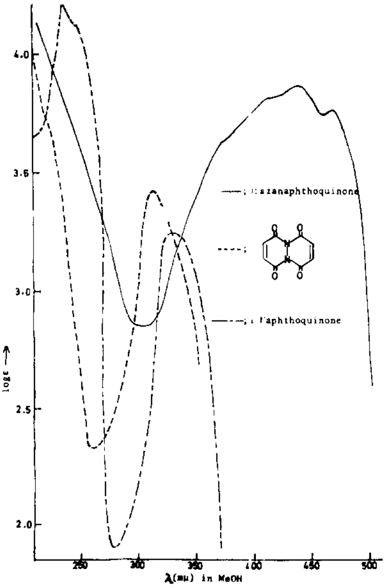
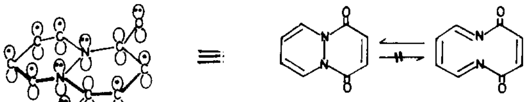
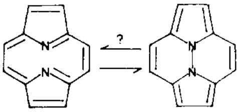


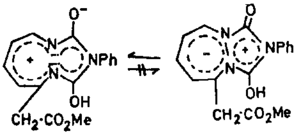
Figure 1.



(V) (VI)



(VII)



(VIII)

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