Pyridazino[4,5-*d*]pyridazine: a New Heterocyclic Ring

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PYRIDAZINO[4,5-*d*]PYRIDAZINE (III) is a heterocyclic ring of very high symmetry, which has never been prepared despite much research on polyazanaphthalene compounds.[1]

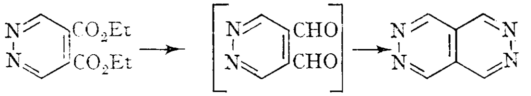
Recently we reported[2] the synthesis of several derivatives of (III), formed by treatment of ethyl ethylene tetracarboxylate and of ethyl pyridazine-4,5-dicarboxylate with hydrazine. Previously only two derivatives were actually known.[3,4]

The unsubstituted ring compound (III) was synthesised by reducing ethyl pyridazine-4,5-dicarboxylate (I) with $LiAlH_4$ at −70° under nitrogen in anhydrous tetrahydrofuran. After decomposition of the excess of $LiAlH_4$ with 50% acetic acid, the filtered solution was added to a methanol solution of hydrazine, and the pyridazine (III) was separated by evaporation of the solution, and purified by vacuum sublimation, followed by crystallization from methanol.

The intermediate of the reaction is believed to be pyridazine-4,5-dicarboxaldehyde (II) as shown by the successive condensation to (III) with hydrazine.

Pyridazine[4,5-*d*]pyridazine is a yellow solid, soluble in water, slightly soluble in ethanol and insoluble in hydrocarbons. It darkens by heating above 250° and melts at about 290° (decomp.).

According to the high molecular symmetry, (D_{2h}), the i.r. spectrum shows a limited number of well resolved and sharp bands with peaks at 3065, 3020, 1530, 1445, 1308, 1290, 1250, 1170, 953, 892, 680, 668, and 478 cm.$^{-1}$ (KBr).



(I) (II) (III)

The u.v. spectra of (III) (Figure) have two structural bands in the range of 225—260 and 265—295 mμ, in addition to a weak band, due to the n–π^* transition, present between 320 and 350 mμ. This band shifts towards shorter wavelengths, as in the pyridazine[5] and phthalazine[6] spectra, as the solvent is changed from non-hydroxylic to hydroxylic.

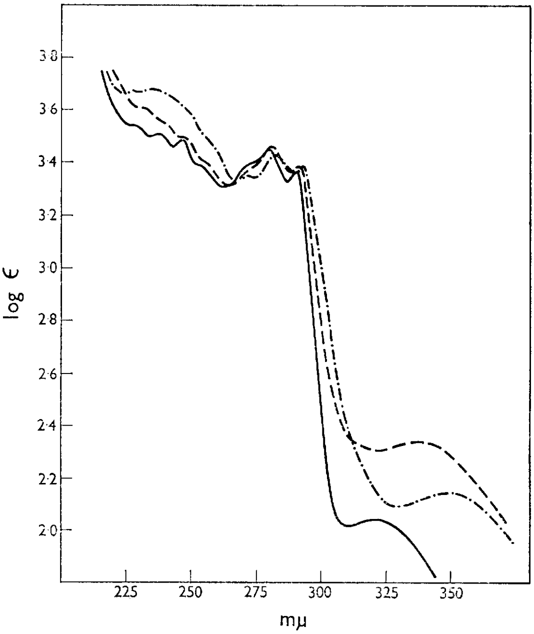


FIGURE. *Ultraviolet spectra of pyridazino*[4,5-d]*pyridazine, in the following solvents:* —— *water,* – – – *methanol,* —·—·— *dioxan.*

The u.v. spectrum in water, unaltered after five days at room temperature, is almost unchanged in dioxan solution; hence, because pyridazino-[4,5-*d*]pyridazine is anhydrous in the solid state, there should not be any appreciable covalent hydration in aqueous solution.

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