Naphtho[1,8-*cd*][1,2,6]thiadiazine

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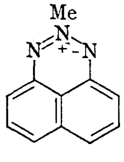
CURRENT interest[1] in sulphur–nitrogen heterocycles and the recent demonstration[2] that the blue product of the methylation of 1*H*-naphtho[1,8-*de*]triazine is 2-methylnaphtho[1,8-*de*]triazine (I) prompted this preliminary report of the preparation of an isoconjugate heterocycle, naphtho[1,8-*cd*][1,2,6]thiadiazine (II).

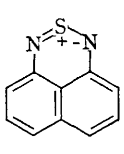
Sachs[3] obtained from 1,8-diaminonaphthalene and thionyl chloride a black infusible solid, $C_{10}H_8NSO$, which was soluble only in pyridine. Reaction of *o*-phenylenediamine with thionyl chloride,[4] sulphur dioxide,[5] or *N*-sulphinylaniline[6] gave 2,1,3-benzothiadiazole. The last reaction involved two moles of *N*-sulphinylaniline and was assumed[6] to proceed by the elimination of aniline and sulphur dioxide from the bis-adduct, *o*-$C_6H_4(NH{\cdot}SO{\cdot}NHPh)_2$ (III).

Sulphur dioxide was not eliminated when 1,8-diaminonaphthalene was heated in benzene with *N*-sulphinylaniline. The sole product was 1*H*,3*H*-naphtho[1,8-*cd*][1,2,6]thiadiazine 2-oxide (IV), m.p. 178–180° (decomp.) (preheated bath), a colourless solid crystallising in plates from benzene. The diamine was regenerated by mild hydrolysis. When (IV) was heated, alone or in a solvent, naphtho[1,8-*cd*][1,2,6]thiadiazine (II) was formed. The heterocycle crystallised in dark plates [m.p. 139–141° (decomp.)] from blue solutions in hydrocarbons ($\lambda_{max.}$ 658 mμ; $\log_{10} \epsilon$ 2·76) in which it was monomeric. Perkins[2] reported $\lambda_{max.}$ 655 mμ ($\log_{10} \epsilon$ 2·76) for the triazine (I).

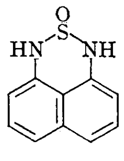
Cava and Schlessinger[1] have suggested that the chemical stability of naphtho[2,3-*c*][1,2,5]thiadiazole, which incidentally had been reported earlier[5] albeit with a different melting point, reflects a significant degree of tetracovalent character of the sulphur atom (Va). Physical studies[7] of 2,1,3-benzothiadiazole, however, imply that the *o*-quinonoid structure (*cf.* Vb) is important in the ground state. Such structures are not feasible for the thiadiazine (II), which was hydrolysed readily by base to 1,8-diaminonaphthalene. In contrast to the similar ultraviolet absorption of (I) and (II), that of 2-methyl-1,2,3-benzotriazole ($\lambda_{max.}$ 274 mμ)[8] is quite different from that of 2,1,3-benzothiadiazole ($\lambda_{max.}$ 310 mμ)[9].



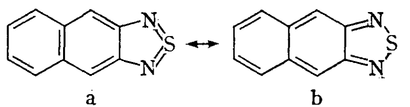
(I)



(II)



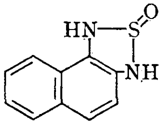
(III)



a

b

(V)



(VI)

The isolation of an intermediate dihydro-oxide VI [m.p. 150–151·5 (decomp.)] from the reaction of *N*-sulphinyl aniline and 1,2-diaminonaphthalene suggests that adducts like (III) are not involved in the formation of thiadiazoles from *ortho*-diamines and *N*-sulphinylamines.

Satisfactory analytical and spectral data have been obtained for the new compounds.

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