An Unusual Bicyclic Oxidation Product of Dithizone

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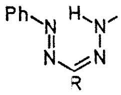
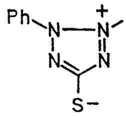
Summary The oxidation of dithizone [3-mercapto-1,5-diphenylformazan, $C_{13}H_{12}N_4S$, (I); R = SH] under alkaline conditions to a sydnone, $C_{13}H_{10}N_4S$ (II), is reversible; however under acid conditions elimination of a proton from the *ortho*-position of one of the phenyl residues leads to a purple isomer with a new bicyclic ring system (IV), the structure of which has been established by *X*-ray structure analysis.

MANY unsuccessful attempts have been made to identify the 'yellow oxidation product' first noted in solutions of the analytical reagent dithizone (I; R = SH) that have deteriorated on keeping.[1] It is certainly not identical with the orange coloured sydnone (II) obtained from (I; R = SH) by the action of manganese(IV) oxide and incorrectly formulated[2] as diphenylthiocarbadiazone (III). This sydnone can also be obtained from dithizone by using other mild oxidants such as pentyl nitrite, potassium ferricyanide, or hydrogen peroxide in dilute aqueous ammonia.[3,4] If oxidation is effected with concentrated hydrogen peroxide in strongly alkaline solution where the dithizonate ion (I; R $=S^-$) predominates, a purple sulphonic acid (I; R = SO_3^-)

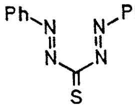
results.[5] A second purple compound of molecular formula $C_{13}H_{10}N_4S$ [$\lambda_{max}(CHCl_3)$ 316 and 524 nm.], isomeric with (II) is formed by the prolonged action of mineral acids on a solution of (I; R = SH) in dioxan[6] but more conveniently by boiling its solution, or that of the sydnone (II) or of diphenylthiocarbazide in glacial acetic acid.[3,4,6] It combines reversibly with a proton to give the green conjugate acid (λ_{max} *ca.* 262 and 680 nm.) but it also dissolves in concentrated aqueous alkali to give a blue solution (λ_{max} 320 and 610 nm.) from which it can be reprecipitated on acidification. The presence of an NH group is shown by an i.r. peak (KBr) at 3270 cm.$^{-1}$ which moves to 2438 cm.$^{-1}$ on deuteriation. These results rule out structure (III) but support the novel structure (IV) in which an *ortho*-proton of one of the benzene rings of (I; R = SH) has been involved in the oxidation. This unexpected result has been confirmed by *X*-ray analysis which shows unequivocably the presence of a binuclear system linked by two nitrogen atoms to an isolated phenyl group.



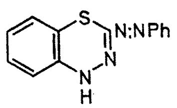
(I)



(II)



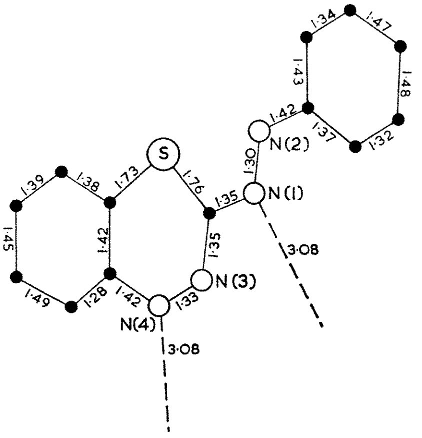
(III)



(IV)

Crystals of the compound are orthorhombic, $a = 15{\cdot}15$ $b = 12{\cdot}00$ $c = 6{\cdot}81$ Å, space group $P\ 2_12_12_1$, $Z = 4$. The structure was determined by Patterson and Fourier methods, based on visual estimation of 567 independent reflexions. After least-squares refinements, with allowance for anisotropic vibrations, R is 10·6%.

A projection of the molecule down ***a*** is shown in the Figure.



FIGURE

The estimated standard deviations of the bond lengths are 0·02—0·03 Å. The shortest intermolecular contact is of length 3·08 Å, between N(4) and N(1). This is close to the average for an N–H · · · N hydrogen bond.[7]

The molecule is approximately planar, no atom deviating more than 0·25 Å from the mean plane.

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